FUEL CELL TECHNOLOGY
A State of the Art

J.D. Pandya and S. Varshney

Tata Energy Research Institute,
7, Jor Bagh,
New Delhi 110003

1985

CONTENTS

Page No

1. INTRODUCTION.............................. 4

2. PROFILE OF FUEL CELL DEVELOPMENT AND PRESENT STATUS............................ 8

3. BASIC PRINCIPLE........................... 23

4. FUEL CELL PERFORMANCE..................... 33
   4.1 Activation or Chemical Polarization........................ 35
   4.2 Concentration Polarization......... 36
   4.3 Resistance Polarization............ 39
   4.4 Heat Transfer in Fuel Cell......... 39

5. FUEL CELL TYPES........................... 42
   5.1 Low Temperature Fuel Cells......... 45
   5.1.1 Alkaline Fuel Cells................ 45
   5.1.2 Acid Fuel Cells.................... 49
   5.2 High Temperature Fuel Cells........ 57
   5.2.1 Molten Carbonate Fuel Cell......... 58
   5.3 Very High Temperature Fuel Cells... 64
   5.3.1 Solid Oxide Electrolyte Fuel Cell.. 64

6. INTEGRATED FUEL CELL SYSTEM.............. 71

7. ADVANTAGE OF FUEL CELL OVER THE CONVENTIONAL SOURCES OF POWER............ 82

8. STATUS OF FUEL CELL RESEARCH AND POTENTIAL APPLICATIONS IN INIDA.......... 91
   8.1 Status of Fuel Cell Research in India.............................. 94
   8.2 Scope of Fuel Cell Applications and Development in India........... 98

9. BIBLIOGRAPHY.............................. 101

List of Tables

1. Thermodynamic characteristics of important fuel cell reactions 27
2. Thermodynamic efficiency of $H_2(g) + 1/2O_2(g) \longrightarrow H_2O(g)$ reaction at various temperatures 28
3. Fuel cell parameters 43
4. Heating value of various fuels 77
5. Characteristics of 40 kW on-site power plant 79
6. Characteristics of 4.5 MW Demonstrator power plant 80
7. Comparison of fuel cell power plants with various electrolytes 81
8. Summary of Energy conversion devices 83
9. A comparison of emissions from conventional power plants with those from an experimental fuel cell operating on natural gas 87

LIST OF FIGURES

1. Profile of fuel cell development and its present status 10

2. Schematic of a phosphoric acid fuel cell ... 24

3. Comparison of Carnot cycle efficiency and ideal efficiency of hydrogen oxygen fuel cell 29

4. Typical cell potential and efficiency vs.current relation of a fuel cell showing regions of major influence of various types of overpotential losses 34

5. Cell voltage vs.operating temperature for different fuel cell types 44

6. Schematic of water transport in the Allis Chalmers fuel cell 48

7. Basic structure of Phosphoric acid electrolyte fuel cell 51

8. Schematic of a molten carbonate fuel cell 62

9. Solid oxide electrolyte fuel cell stack 68

10. Schematic of Integrated fuel cell system ... 72

11. Efficiency comparisons of common modes of on-site power generation 84

12. Part load efficiency characteristics of fuel cells 85

13. Total fuel cell efficiency 88

1.0 INTRODUCTION

Most of our useful energy is obtained from the conversion processes:

Chemical energy-->heat-->mechanical energy--> electrical energy

or chemical energy--> heat-->mechanical energy

These routes provide the basis for operation of the steam turbine electric power station and for the operation of the internal combustion engine. These conversion processes transform energy stored within the chemical bonds of hydrocarbon fuels such as coal, oil and natural gas to heat energy after combustion. The maximum amount of useful power that can be obtained from this energy is that which a Carnot engine would obtain operating between the temperature at which the heat energy was released and in general, the surrounding temperature. In a power plant the various conversion processes limit the system to an overall efficiency of at best, about 30 per cent.

A fuel cell is an electrochemical device consisting of an anode, a cathode and an electrolyte in which the chemical energy of a conventional or non-conventional fuel is directly and efficiently converted into low voltage direct current electric energy. This low voltage direct current power output can be multiplied by connecting a number of cells in series or parallel arrangements to get the desired voltage. The specific reaction varies depending upon the type of cell, but essentially the fuel is dissociated catalytically and electrons are released to provide direct electric current. Unlike other batteries, the fuel cell does not consume its electrode in this process but instead uses up fuel and oxidant, fed continuously from outside the cell. It has no high speed moving parts and can capture nearly all the energy generated by the oxidation of fuel. A variety of fuel such as hydrogen, methanol, ethanol, natural gas, fuel oil, biogas etc. can be utilized directly or indirectly after suitable modification.

A fuel cell power plant consists of various subunits such as fuel processor, fuel cell subsystem, power conditioner and thermal management subsystem. Various types of fuels like coal, oil, natural gas are processed by the fuel processor to generate hydrogen. Since it is the primary fuel for the system, fuel cell subsystem electrochemically coverts the fuel in to direct electric current, which is converted to A.C.current by the power conditioner. Thermal management subsystem efficiently utilises the heat generated during the electrochemical reaction, thus increasing the overall efficiency of the system. One of the major advantages of such a device is that, since the electrochemical oxidation can be carried out isothermally, the

Carnot limitation on efficiency does not apply. Moreover, the fuel cell eliminates the high temperature combustion and the associated mechanical to electrical conversion processes found in all energy conversion systems to produce electrical power.

The efficiency of a fuel cell power plant can, therefore, be much higher than any conventional power plant. A coal fired thermal power plant operating under optimal conditions can yield 35 percent efficiency. A nuclear power station can at best attain 30 percent efficiency. But, a fuel cell not only generates electricity at 40 percent efficiency but its end products (hot water and steam) can also be harnessed to generate additional power, thus the overall efficiency of the fuel cell power plant adds up to between 70 and 80 percent. However, the design problems have not yet been completely solved, but the solutions to these problems are within sight.

This paper deals with the state of the art of fuel cell technology. The profile of fuel cell development and its present status is described. The basic principle and the factors limiting its performance have been dealt within the subsequent sections. The various types of fuel cells that have developed over the years have also been classified and described. An integrated fuel cell power plant, the potential fuels for it, as well as the salient features of this system are also described. Lastly, the paper discusses the status of fuel cell research and its potential applications in India.

2.0 PROFILE OF FUEL CELL DEVELOPMENT AND PRESENT STATUS

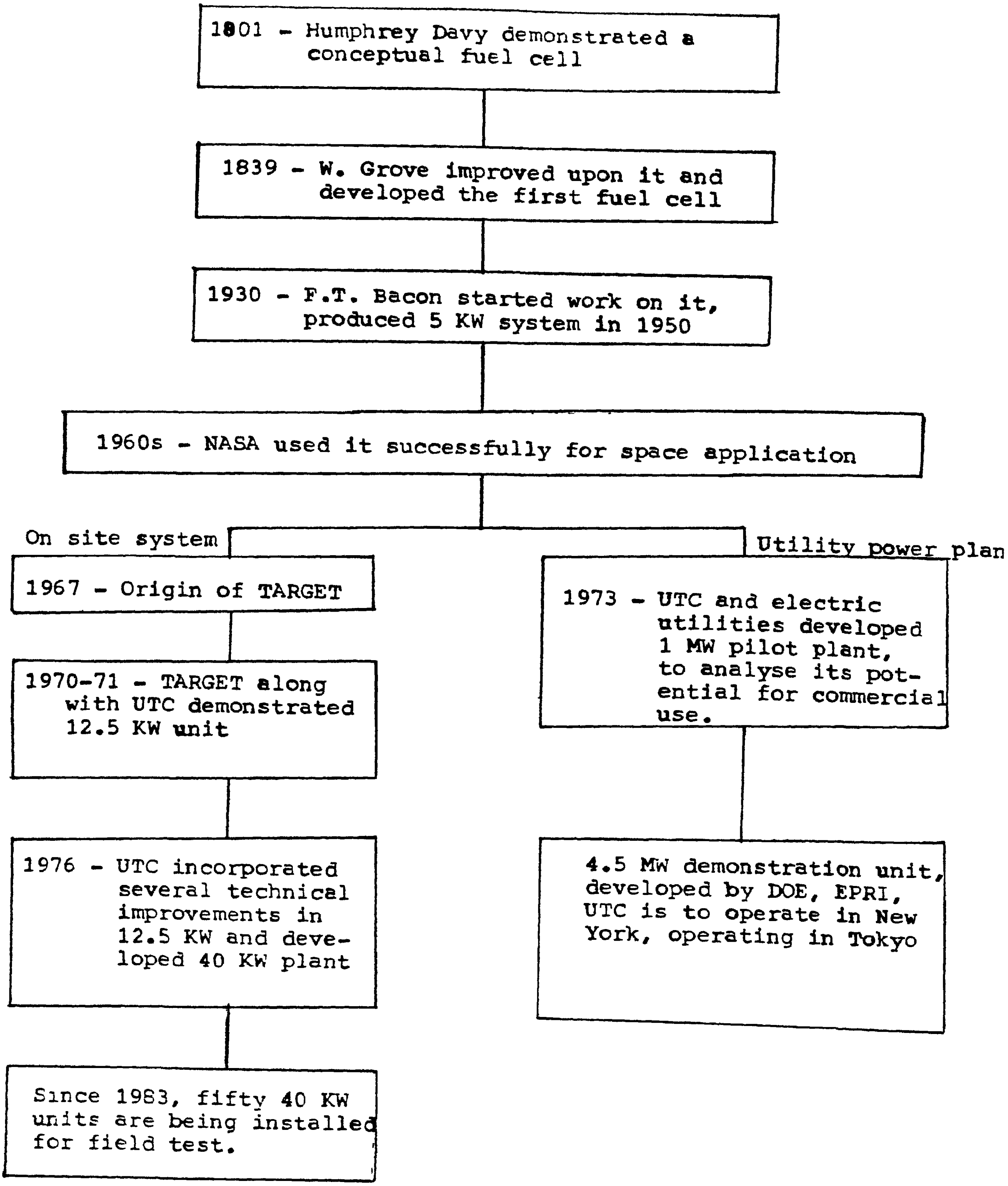
The concept of the direct conversion of chemical energy to electrical energy is not new. It dates back to the investigation of Galvani (1737-98) and Volta (1745-1827) whose names are associated with electrical phenomena. In 1801, Humphrey Davy, one of the pioneers in electrochemical research, demonstrated a conceptual fuel cell that used carbon and nitric acid. In 1839 in Britain, Sir William Grove first invented the fuel cell and called it the gaseous battery, to distinguish it from another invention, the electric storage battery. The fuel cell technology lay fallow for many years until an engineer at Cambridge University, Francis T.Bacon, began working on it in the 1930's, eventually producing a 5 kW cell in the 1950's. The U.S. National Aeronautics and Space Administration (NASA) adopted the fuel cell in the early 1960's as the power source for various spacecrafts. The most successfully demonstrated fuel cells to date are the 1 kW Gemini, 1.5 kW Apollo (between 1960-1970) and the 7 kW Space Shuttle Orbiter (in 1980) (Linden,1984).

Figure 1 gives the profile of fuel cell development and its present status. Since late 1960's, development of fuel cell as a utility power plant has taken place in the USA. It has proceeded along two lines:

(i) power plants for on-site applications (eg. residential and office buildings);

(ii) utility power plants.

In 1967, the American Gas Association in collaboration with electric utilities formed the Team to Advance Research on Gas Energy Transformation (TARGET) program to develop small 12.5 kW fuel cell generators for individual residential and commercial use. These were intended to supply both electricity and domestic heat in a cogeneration mode. A major breakthrough occured in 1968-69 when graphite was shown to be a satisfactory cell construction material, since its corrosion rate is exceptionally low even at the oxygen cathode at 200^{o}C. With the telfon-bonded electrode structure improvements, 0.5 mg/cm^{2} of platinum was shown to be as active as 20mg/cm^{2}. During 1971-73, Target in cooperation with United Technology Corporation (UTC) developed a 12.5 kW onsite power plant which demonstrated an electrical efficiency of 28%. In the early 1970's, a test of 65 of these (12.5 kW) onsite phosphoric acid fuel cell power plants at 35 sites in the U.S.A., Japan and Canada demonstrated their technical feasibility. All functions required for onsite and utility generation were demonstrated in these field tests. Although these power plants proved to be inadequate in cost and durability, they provided valuable information on commercial prospects and identified areas where additional technology and component developments were needed.



1801 - Humphrey Davy demonstrated a conceptual fuel cell

1839 - W. Grove improved upon it and developed the first fuel cell

1930 - F.T. Bacon started work on it, produced 5 KW system in 1950

1960s - NASA used it successfully for space application

On site system

1967 - Origin of TARGET

1970-71 - TARGET along with UTC demonstrated 12.5 KW unit

1976 - UTC incorporated several technical improvements in 12.5 KW and developed 40 KW plant

Since 1983, fifty 40 KW units are being installed for field test.

Utility power plan

1973 - UTC and electric utilities developed 1 MW pilot plant, to analyse its potential for commercial use.

4.5 MW demonstration unit, developed by DOE, EPRI, UTC is to operate in New York, operating in Tokyo

Figure 1: Profile of Fuel Cell Development and Its Present Status

Following the 2.5 kW tests, TARGET and UTC developed a relatively sophisticated 40 kW experimental unit, which incorporated heat recovery and several technical improvements, reflecting lessons learned from the previous tests. This power plant fueled with natural gas achieved total efficiency of 80%.

In 1976, the U.S. Department of Energy in cooperation with TARGET initiated a programme to upgrade and improve these 40kW phosphoric acid power plants. The programme incorporated recent technological improvements and heat recovery provision into an improved highly sophisticated 40 kW design, suitable for pre-commercial field test. Emphasis was laid on lowering the cost and improving the reliability of all power plant components. The Gas Research Institute (GRI) assumed the gas industry's TARGET involvement in the programme since 1976, when it originated. In 1982, two experimental prefield test 40KW phosphoric acid onsite fuel cells were installed. These experimental units which tested and verified the hardware specifications, demonstrated the ease of installation. The pilot plant exceeded 18000 hours of operation, more than 8000 hours with one fuel cell power plant and with a continuous run of more than 3000 hours with another (Linden,1984). Besides, no failure due to fundamental problem in the major high technology substation had occured. However, component reliability and the quality of water in the cooling system of the power plant caused concern. So a number of potential solutions were identified for the above problem for incorporation into the field test units (Busby,1984).

Since the design and engineering development were complete, a jointly funded GRI/DOE contract was issued in January 1982 to UTC, to manufacture and to field test onsite fuel cell system programme. (In the systems manufactured by UTC, heat is removed by the circulation of water vapour through stack coolant passage.) The first eleven, 40 kW PAFC field test power plants were installed recently (started in October 1983 - April 1984) at various places like restaurants, apartment complexes, health clubs etc. as a part of the programme that have continued through 1985 and will install 39 more such units. The initial data obtained from the first several field test units indicate an improvement in the quality of water in the cooling system of the power plant. The most successful of the field tests according to GRI is the one in Portland, Oregon. It has logged over 3300 hours of successful operation (Marshall,1984). But the ones in California and Maryland had faced some problems. In an effort parallel to the field test project, UTC, under contract with both GRI and DOE is investigating several advanced and efficient cathode catalysts (Busby,1984). In addition, better methods of controlling the loss of phosphoric acid electrolyte and periodically replenishing it in the field tests are being developed. Parallel development efforts were initiated at Westinghouse and Engelhard. Their activity was focussed on PAFC cells, stack development and verification, component design and system conceptualization. Westinghouse/Energy Research Corporation (ERC) use a potential distributed gas (DIGAS) cooling concept that allows a portion of the reactant's air stream to pass through coolant plates. The Engelhard efforts are focused on smaller power plants (5-12 kW) for industrial or traction applications using methanol as the fuel (Linden,1984). It has tested 5 kW methanol air integrated PAFC system as part of an ongoing development programme and is also working on improved Platinum electrocatalyst.

In an effort parallel to the on-site field tests of the fuel cell system, 10 electric utility companies joined with UTC in 1971 to analyze the potential of this technology for commercial electric generation. In 1973, a programme designed to advance fuel cell power plant technology from kilowatt size units to Multimegawatt units for commercial service led to the manufacture and test of 1 MW pilot plant unit at UTC's facility in South Windsor, Connecticut. It was successfully operated for more than 1000 hours and generated about 700,000 kWh

(Bell,1980). The next phase of the electric utility programme to bring fuel cells to commercial use was the 4.5 MW fuel cell Demonstration Project, which was initiated in 1976 with an agreement among the DOE, EPRI and UTC (Bell,1980). It is built in Central Manhattan on a site provided by the Consolidated Edison Company of New York. It is installed next to Consolidated Edison's East River Generating Station, a site selected to demonstrate that fuel cell power plants can be sited in higher load urban areas with stringent environmental constraints. So far it has not been successful in producing electricity. Its installation and testing were slowed down by licencing regulations and by the fire department's uncertainties concerning untested aspects of the new technology, particularly with respect to fuel storage and processing area and in certain aspects of hydrogen handling. This required pressure testing of parts of the system, including that of the one-of-a-kind advanced sheet-metal heat-exchangers, some of which were irreparably damaged by the freezing of water used for hydraulic testing during very cold weather. In consequence, installation of the stored power sections was not completed until the end of 1983, by which time the 1976 vintage technology cell stacks had exceeded their electrolyte storage inventory lifetime, so this was a failure. UTC is planning its next venture, the 11 MW plant, which will incorporate certain improvements on the 4.5 MW design. Most recently in 1982, Westinghouse and ERC started work on a 7.5 MW PAFC power plant. This system uses air cooled DIGAS System instead of expensive water-cooling (as was developed by UTC) (Marshall, 1984). Westinghouse has chosen its test site with caution, unlike UTC it has not selected freezing climate or an inner city and has decided to instal its 7.5 MW plant in Southern California by mid-1987. At present the activities related with the transition from demonstration to commercialization are being coordinated by the fuel cell user's group which was formed in 1981 (Landgrebe, 1981).

In addition to actual engineering developments and demonstrations of first generation (phosphoric acid) fuel cell, beginning in 1971, studies and development of a technology base for high temperature, second generation (molten carbonate and solid oxide) fuel cell power plants have been initiated in conjunction, by EPRI, UTC, DOE and GRI. The main incentive for development of these cell-systems is the expectation that favourable electrode kinetics at high temperature will permit the use of inexpensive catalyst material. Also, it has been assumed that fossil fuels may be reacted directly at high temperature and thus make the system less expensive and convenient.

In Japan, the motivation for licensing the U.S. utility fuel cell technology was prompted by the high density population. The national research and development programme on fuel cell power generation, which belonged to °Moonlight Project', was initiated in August 1981. Mitsubishi Electric, Hitachi, Toshiba and Fiji are the contractors to the New Energy Development Organization under the "Moon-Light Project". The fundamental research carried out reveals that the key issues with respect to the cell life are corrosion of the fuel cell components and electrolyte management. Fuel Cells are expected as a fourth electric power source succeeding to hydro, thermal and nuclear electric power generations. It is expected that the PAFC will be commercialized in the electric power industries market around 1991 and will be installed for replacement of oil burned thermal power stations which will have lasted their lives. The research program in Japan has been directed towards exploring and developing techniques for highly reliable fuel cell systems. The Energy Saving and Conservation Department of Industrial Technology Council approved a proposal that both low temperature and low pressure type, and the high temperature and high pressure type plants be designed, manufactured and constructed in the period 1984-85 and tested in 1986. The targets of voltage and current characteristics of the cells were set up at 0.7 V (at 200 mA/cm^2) for the LT/LP type and 0.68 V (at 220 mA/cm^2) for the HT/HP types. The quantities of platinum catalyst were set up at 6.5 g/kW as the target. The Government Industrial Research Institute, Osaka has undertaken research in the area of novel cell materials for the molten carbonate fuel cells as also for the solid oxide fuel cells.

The Tokyo Gas Company and the Osaka Gas Company participated in the TARGET project in 1972 and both companies started field tests of on-site/integrated energy systems of PAFC PC-18 in March 1982. The present major fuel cell power plant project has been completed by the Tokyo Electric Power Company in the Goi thermal power station campus at Chiba-ken. All process and control systems were tested in November 1982 and the cell stack assembly was connected to the plant. The Goi unit ordered from UTC ran for the first time in April 1983 and after some maintenance work in 1984, it has been operating satisfactorily to produce 4.8 kW as designed for (Marshall, 1984). Upto March 1985, the plant had run for 1900 hours and had produced 4200 MWh. It uses natural gas to generate electricity with an efficiency of 40% without and 80% with waste heat recovery. Japanese Government and Hitachi are also running a project on direct methanol fuel cell for transport. Besides, ten Japanese Companies are participating in the Ministry of International Trade and Industry (MITI) and Agency of Industrial Science and

Technology (AIST) national R & D program on fuel cells.

Fuel cell developments in Europe have been very modest in comparison and mainly concentrated on the alkaline fuel cell, since Europeans so far have been interested in the use of fuel cells only for transport. Siemens in West Germany have been pursuing the development of the H_2/O_2 alkaline fuel cell since the mid-sixties. A report (Gallagher,1983) mentioned the testing of three 7.5 kW fuel cells in a laboratory simulation of a hospital standby power system. The system includes lead acid batteries for start up.

Elenco - a Belgium/Dutch consortium founded in 1976 by three stockholders (two from Belgium, one from Netherlands) has adopted a pragmatic approach in the field of developing and implementing fuel cells in the commercial vehicle market (Gallagher, 1983). It has chosen the hybrid power source approach so as to be able to use the fuel cell mostly at constant power level. It has developed the electrodes and stack technology with mass production in mind. A van became operational in November 1982 and until now no influence of the driving conditions has been experienced by the module performances. The feasibility studies for city bus and garbage truck applications have been found to be very favourable and the first buses and trucks are expected to be ready for testing in 1988 or 1989. Elenco is also involved in the scaling up of its fuel cells and the largest one operated so far is the 12 kW fuel cell of the van. At present, a 40 kW cell is under construction for the Belgian Geological Service which plans to use the system to provide power for its drilling and measurement equipments at all possible underground sites in Belgium.

In Italy, work on acid fuel cell for transport has been carried out at the Fiat Research Centre. Test results with a Fiat 242 elctric van demonstrated that an integrated system of metal hydride storage and fuel cells characterised by an energy density of 110 Wh/kg, allowing 3 h of operating range at a top speed of 70 km/h (Gallagher,1983). Following feasibility studies in 1981, a research program for testing of a 2.5 kW PAFC has been initiated. The main results obtained so far include the determination of minimal maintenance needed to preserve overall system performance, steady-state electrical characteristics and values of total and partial stack voltages as a function of time during sudden load rises and drops. Recently, the research attention is also directed towards preliminary material studies for MCFC electrodes, processes for SOFC and high protonic diffusivity. Basic research, demonstration and construction of prototype of 50 kW MCFC plants are being planned for the period 1985-90.

In France, the advantages of economy and the reduction of harmful effects were the deciding arguments that led Institut Francais des Petroles (IFP) to undertake research on this new source of energy conversion in 1959. Since then, it has concentrated on basic research areas, related to acid and alkaline fuel cells (Grehier,1979).

Though no major work has been done in UK, two distinct fuel cell applications have been identified: transport, which requires fuel cells that work at temperatures below 100°C and base-load power generation utilizing coal gas. The Central Electricity Generating Board studies have indicated that in the post 2000 era, an intermediate temperature (600-800°C) fuel cell operating in a coal-fuelled integrated system could provide an attractive option for power generation. Research activities to meet the requirements in the time frame available are in the stage of planning.

The fuel cell programme in Denmark is directed towards the development of advanced solid state fuel cells. The Energy Research Laboratory (ERL) and the Odense University are engaged in a collaborative project to develop and evaluate solid state protonic conductors as electrolytes in these systems. The problems of these materials have been identified over the period of years through scientific papers presented in the workshop by

ERL. A mutual project between ERL, Inorganic Chemistry Laboratory, Oxford and Sorapec, Paris on "Materials Research for Advanced Solid State Fuel Cells" is expected to begin in early 1986.

Brazil's interests for fuel cells are in its applications in the remote areas to replace diesel generators for telecommunication stations as emergency generators and in hybrid cars. Work is going on at present in four laboratories. The evaluation of methanol and ethanol as fuels has been undertaken at the University of Ceara alongwith the objective of studying components and materials for fuel cells. A 200 W PAFC prototype is being developed. At Rio de Janeiro, a 150 W alkaline fuel cell prototype was put in operation in 1983. The major thrust is to optimize the electrode performance. The Instituto de Pesquisas Technologicas has attempted to develop a process to obtain hydrogen from methanol. At San Carlos, a 50 W PAFC prototype has completed 100 hours of continuous operation without any failure. The construction of 1 kW prototype PAFC on this basis has been planned.

Besides the share in Elenco, the fuel cell research in Netherlands is likely to take off if the Government finds some public utility to fund the R & D programme in the 1:1 ratio. The research is being planned in the area of MCFC technology and the investment is likely to be around 60 million Dutch florins for a five year period.

In China, no major units have been planned though two units producing about 500 W each are running quite successfully. These have basically been used to power residential utilities in remote areas.

In India, there have been no efforts as yet to plan any work in the area of applications of fuel cells for power generation. Some work limited to the laboratory have been carried out by the Central Electrochemical Research Institute in the area of alkaline H_2-O_2 fuel cells. At the Tata Institute of Fundamental Research, a group is working in the area of biochemical fuel cells. It appears that a site specific techno-economic analysis through field demonstration project needs to be undertaken to assess the feasibility of fuel cell technology in Indian context. A proposal for such a work has been put forward by the Tata Energy Research Institute.

3.0 BASIC PRINCIPLE

A fuel cell operates electrochemically or more literally "chemico-electrically" as shown in Figure:2. This cell is actually a reactor, wherein hydrogen as the feed stream or fuel is conducted into the empty space paralleling the porous, electric conducting anode. This anode can be made of porous carbon with a metal catalyst like platinum, which chemically changes the hydrogen atoms to positively charged hydrogen ions and electrons.

$$H_{2(g)} \xrightarrow{\text{anode}} 2H^{+} + 2e^{-} \qquad ....(1)$$

The electrons leave the anode, perform electrical work and enter the cathode. Meanwhile, the positively charged hydrogen ions migrate through the electrolyte attracted by the electronegative oxygen from the cathode. To complete the reaction, the oxygen pulls in the electrons from the outer circuit and water is generated and discharged from the cell.

$$2H^{+} + 1/2O_{2(g)} + 2e^{-} \xrightarrow{\text{Cathode}} H_2O + \text{Heat} \qquad ....(2)$$

The electrical work done by a fuel cell (W_{el}) is given by the amount of charge that flows from the cell multiplied by the driving force that causes it to flow the potential difference of the cell V^{o}. The amount of charge is given by the product of the number of moles of electrons involved in the cell reaction times the number

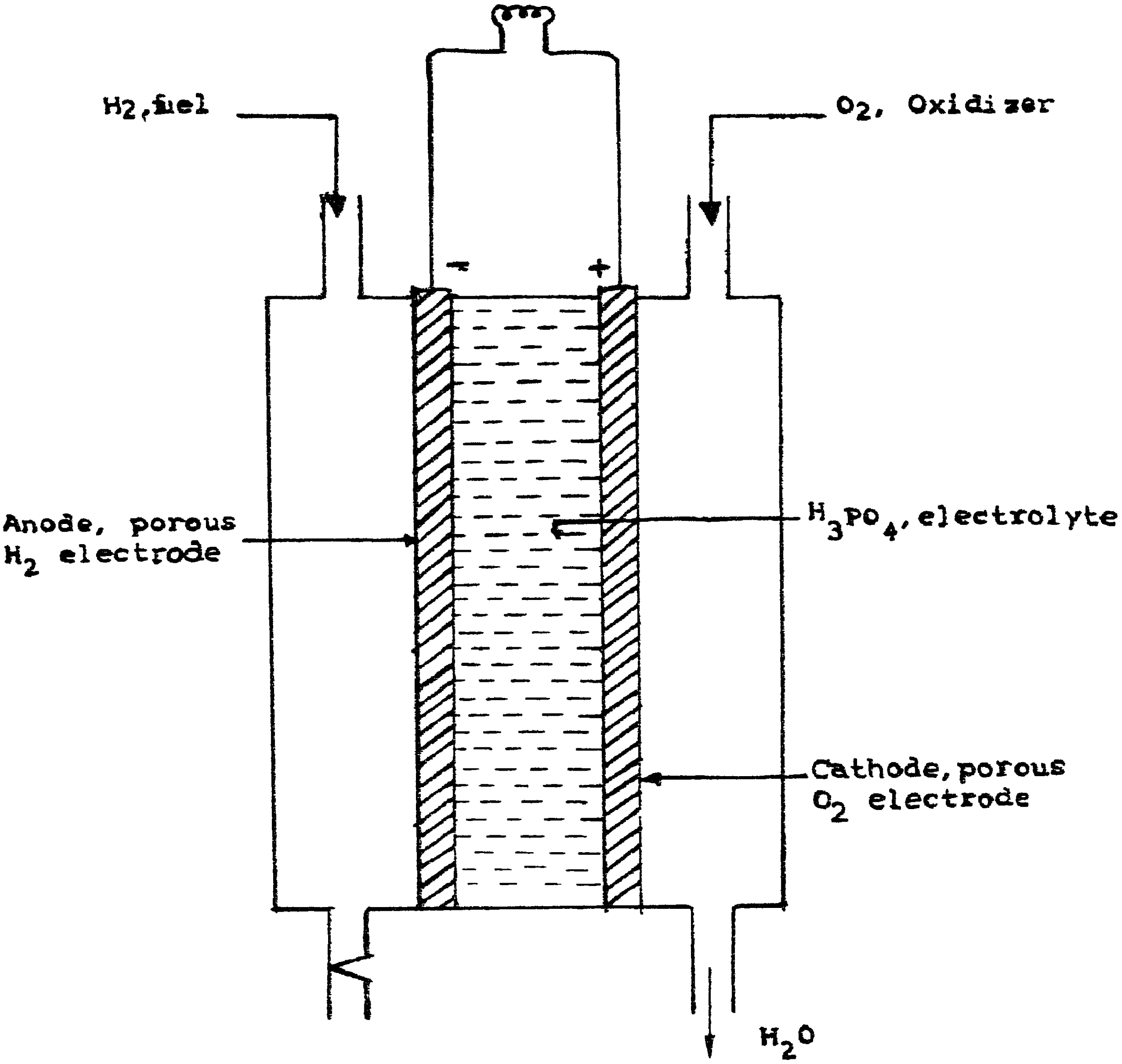

H_2, fuel
O_2, Oxidizer
−
+
Anode, porous H_2 electrode
H_3PO_4, electrolyte
Cathode, porous O_2 electrode
H_2O

Figure 2 : Schematic of a phosphoric acid fuel cell

of coulombs per mole of electrons. Thus,

$$W_{el} = nFV^{o} \qquad ....(3)$$

where n represents the number of moles of electrons transferred from anode to cathode during one act of the overall reaction, F is the Faraday constant. For a steady gas flow fuel cell system in both temperature and pressure equilibrium, it can be shown that the maximum useful work is equal to the decrease in Gibbs free energy, i.e.

$$W_{max} = W_{el} = -\Delta G \qquad ....(4)$$

combining equations (3) and (4)

$$\Delta G = -nFV^{o} \qquad ....(5)$$

The potential difference V^{o} in equation (5) is the reversible potential of the cell, that is the potential measured under open circuit conditions.

The Gibbs free energy is defined as

$$G = H - TS \qquad ....(6)$$

where h,S, and T are enthalpy, entropy and temperature respectively. At constant temperature, the change in Gibbs free energy is

$$\Delta G = \Delta H - T\Delta S \qquad ....(7)$$

Where ΔH is the enthalpy change for the fuel cell reaction, often called the heat of reaction or heat of combustion. This enthalpy change is the heat energy supplied when fuel is burnt in the conventional manner. ΔS is the entropy change for the process and for the reversible process the quantity $T\Delta S$ represents the isothermal heat transfer. The fuel cell utilizes exothermic reaction and thus rejects heat. From the second law of thermodynamics, heat rejection results in the decrease in entropy. For most chemical reactions of interest both ΔG and ΔH are normally negative and thus the decrease in entropy associated with a heat rejection causes ΔG to be numerically smaller than ΔH. The quotient $\Delta G/\Delta H$, therefore, provides a measure for the thermal efficiency of the fuel cell (Angrist,1982).

$$\eta_{ideal} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \qquad ....(8)$$

It determines the thermodynamic limits to which the heat of combustion can be recovered as electric energy. The ideal efficiency of a fuel cell is always less than unity, even in a cell operating reversibly, so long as heat ($T\Delta S$) is being rejected. Table 1 lists the Thermodynamic characteristics of important fuel cell reactions.

Table 1: Thermodynamic Characteristics of Important Fuel Cell Reactions

Reaction	T(°K)	ΔG (kJ/mol)	ΔH (kJ/mol)	Efficiency ideal(%)
$H_2 + 1/2\ O_2 \text{-->} H_2O(L)$	298	-237	-285	83.15
$\text{-->} H_2O(G)$	298	-229	-242	94.6
$\text{-->} H_2O(G)$	773	-203.5	-246	82.7
$2/3NH_3 + 1/2O_2 \text{-->} 1/3N_2 + H_2O(G)$	298	-226	-253.9	89
$1/2N_2H_4 + 1/2O_2 \text{-->} 1/2N_2 + H_2O(L)$	298	-312	-317.9	98.14
$C + O_2 \text{-->} CO_2$	298	-394	-403.8	97.5
$\text{-->} CO_2$	773	-396	-397.5	99.6
$\text{-->} CO_2$	1273	-396	-397.2	99.6
$CO + 1/2O_2 \text{-->} CO_2$	298	-257	-282.6	90.9
$\text{-->} CO_2$	773	-215	-283	75.9
$\text{-->} O_2$	1273	-172	-281	61.2
$1/2CH_3OH + 1/3O_2 \text{-->} 1/2CO_2 + H_2O(L)$	298	-704	-726	96.9
$1/2CH_4 + O_2 \text{-->} 1/2CO_2 + H_2O(L)$	298	-802	-803	99.8
$H_2O(G)$	773	-800	-801	99.8

It is interesting to observe the changes in the thermodynamic efficiency of a simple hydrogen-oxygen fuel cell as its operating temperature is raised from 298°K to 2000°K. Table II lists the functions ΔH^o and ΔG^o, the standard heat of reaction and the change in Gibbs free energy for the reaction

$$H_{2(g)} + 1/2O_{2(g)} \text{-------->} H_2O_{(g)} \quad ....(9)$$

The Carnot efficiency for an engine that operates between the given temperature, T_H, and a sink temperature of $T_c=298^oK$ can be calculated from

$$\eta_{Carnot} = 1 - \frac{T_c}{T_H} \qquad ....(10)$$

Table 2: Thermodynamic Efficiency of $H_{2(g)} + 1/2\ O_{2(g)}$ ------> $H_2O_{(g)}$ Reaction at Various Temperatures

Temperature (^oK)	ΔG^o (kJ/mole)	ΔH^o (kJ/mole)	Efficiency ideal(%)	Carnot efficiency (%)
298	-229	-242	94.5	0
500	-218	-243	89.9	40
750	-205	-245	83.8	60
1000	-192	-247	77.8	70
2000	-134	-251	53.6	85

It can be seen from Figure:3 that the hydrogen-oxygen reaction would provide a fuel cell system potentially far more superior in efficiency to any conventional heat engine system at temperatures below about 850°C. Above that temperature the fuel cell system shows no advantage; in fact the conventional power station would probably be more effective.

The efficiency defined by equation (8) represents the thermal efficiency of the fuel cell alone and does not include losses that would be associated with the attendant accessories required in real installation. In

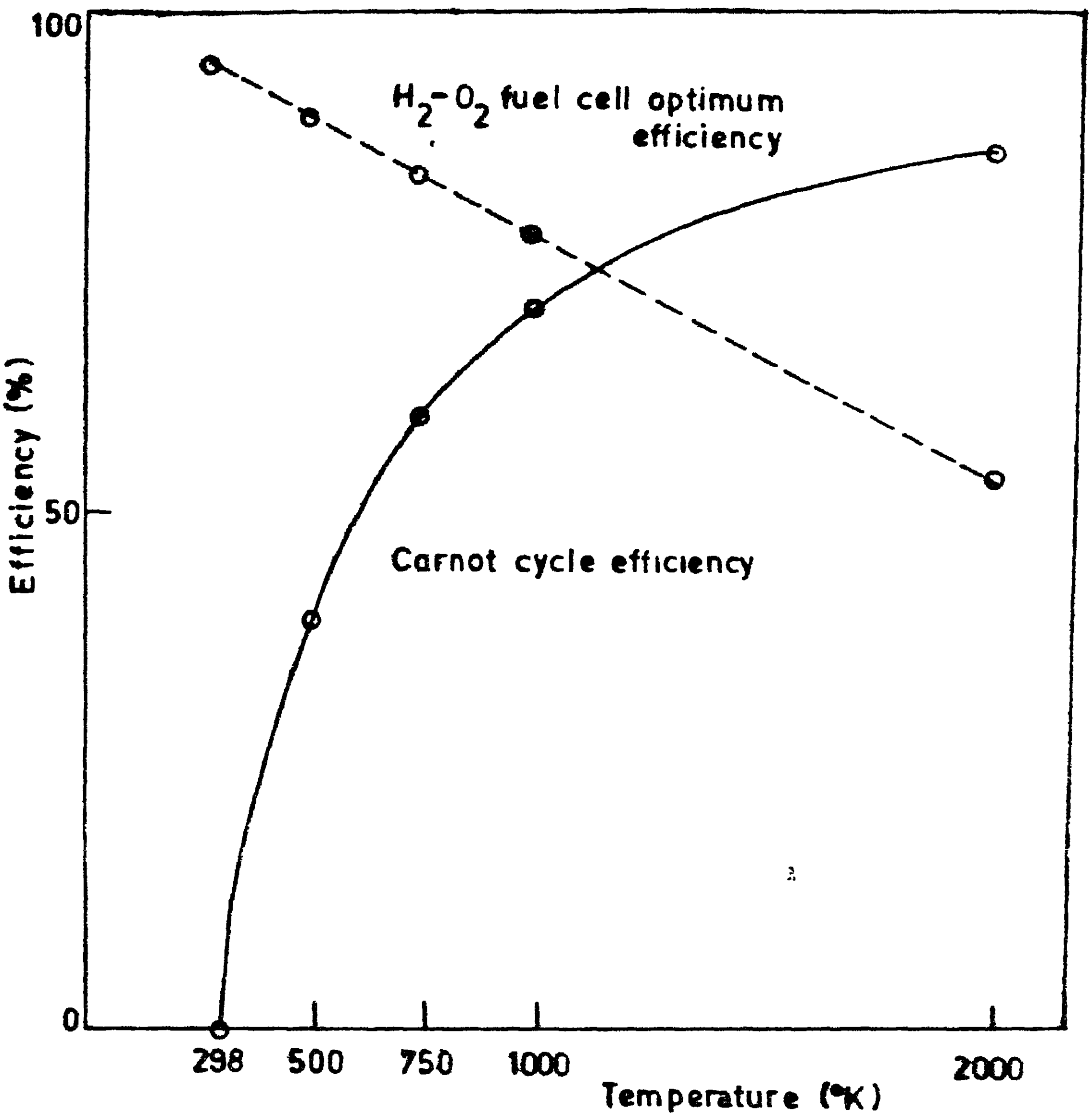


Figure 3 : Comparison of Carnot cycle efficiency and ideal efficiency of hydrogen-oxygen fuel cell.

terms of the reversible electromotive force of the cell the efficiency given by equation (8) is simply

$$\eta_{ideal} = \frac{\Delta G}{\Delta H} = \frac{-nFV^{o}}{\Delta H} \qquad ....(11)$$

In a fuel cell under load, the actual electromotive force that drives the electrons through the external circuit will fall below V^{o} to some lower value V_{ac}. The reasons for this drop are generally attributed to one or more of the following (Carl,1968).

(1) An undesirable reaction at the electrode or elsewhere in the fuel cell.

(2) A hinderance to the reaction at the anode or cathode.

(3) A concentration gradient in the electrolyte or in the reactants.

(4) Joule heating effect associated with the IR drop in the electrolyte.

These undesirable effects lead us to define an actual efficiency as

$$\eta_{actual} = \frac{-nFV_{ac}}{\Delta H} \qquad ....(12)$$

By combining the definition of the actual work, the maximum useful work and the first law of thermodynamics, it may be shown that the difference between the two work expressions must appear as rejected heat. This rejected heat is the heat that must be removed from the cell if the reaction is to proceed isothermally. This quantity will be larger than the reversible isothermal heat transfer TΔS. Thus, another measure of efficiency can be obtained by dividing equation (12) by equation (11).

$$\eta_{ac} = \frac{V_{ac}}{V^{o}} \qquad \text{.......(13)}$$

Since generation of an electrical current is determined by the rates of the electrode reactions, the current density which is the current per unit active area of the surface of an electrode, can be obtained from thermodynamic considerations alone. However, the efficiency defined by equation (13) decreases as the current density increases and therefore, can be used as a convenient index to measure the irreversibilities of the fuel cell.

Finally, the faradaic or current efficiency, η_f, is used to define the fraction of the reaction which is occuring electrochemically to give current. It should be considered separately for each electrode since the fuel consumption may not equal the oxidant consumption. However, for simplicity, just one expression for faradaic efficiency is written:

$$\eta_f = \frac{I}{nFN_{fu}} \qquad \text{.......(14)}$$

Where N_{fu} is a total number of moles of fuel reacted electrochemically per second. The quantity $(1-\eta_f)$ is the fraction of the reactants that may react directly to give heat release in the cell or may react to products other than those desired. The part of the chemical free energy that actually results in electrical energy is $\eta_v \eta_f$.

4.0 FUEL CELL PERFORMANCE

As seen earlier it is possible to have at least theoretically, 94% conversion efficiency of the fuel cell. But practical cells using pure hydrogen and oxygen generally have conversion efficiency of 40%.

The performance of a fuel cell is represented by the current density vs. voltage (or polarization) curve. The theoretical emf or voltage of a fuel cell can be calculated from the Gibbs free energy change (equation 5). For the hydrogen-oxygen cell at 25°C with the gases at atmospheric pressure the ideal emf is 1.23 volts. For the moderate currents at which fuel cells normally operate the emf is 0.7 to 0.8 volt. The voltage losses from the ideal are referred to as polarization (as illustrated in figure:4) and are generally classified into three categories

(1) activation or chemical polarization;
(2) concentration polarization
(3) Ohmic or resistance polarization

The actual cell voltage V_{ac} can be written as:

$$V_{ac} = V^o - \Delta V_{chem(c)} - \Delta V_{conc(c)} - \Delta V_{chem(a)} - \Delta V_{conc(a)} - \Sigma IR \qquad ....(15)$$

Where V^o is the ideal potential and subscripts c and a denote cathode and anode respectively. The magnitude of

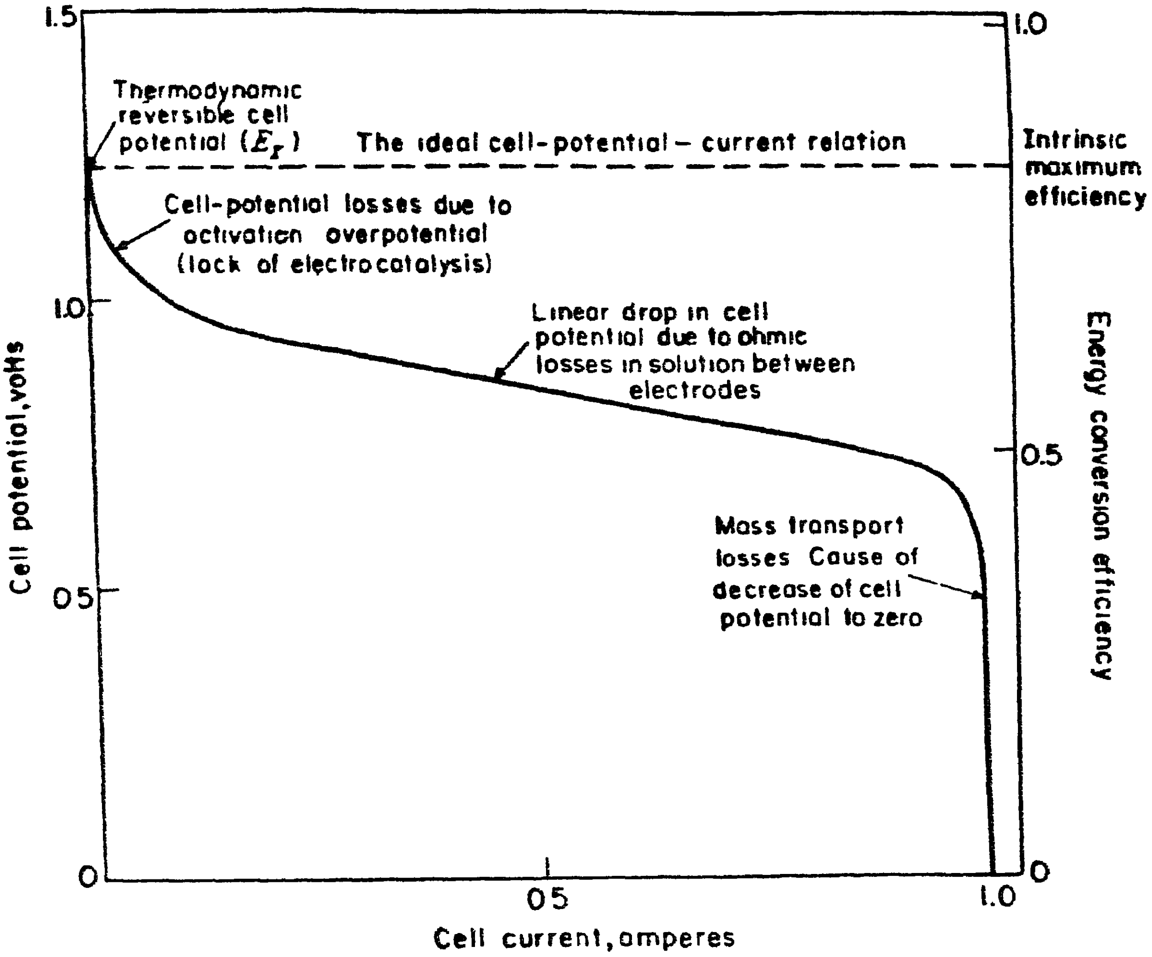


Figure 4: Typical cell potential and efficiency vs. current relation of a fuel cell, showing regions of influence of various types of overpotential losses (Bock~is, 1969)

each type of potential losses increases with current density drawn from the cell, hence, the cell potential and the efficiency of the cell decreases with the increasing current density.

4.1 Activation or Chemical Polarization:

It is a surface phenomenon, the magnitude of which depends in part upon how ions are discharged at the electrodes and in part upon the rate at which they are discharged. The electrochemical oxidation of fuel involves a chemisorption process in which the adsorbed molecules (those collected on the surface) are held to the surface by bonds comparable to those that form in the production of chemical compounds. The fuel gas engages in chemisorption either as molecules or atoms while electrons are removed from the adsorbed atoms. This involves a breakage of the molecule bonds and formation of new bonds between the fuel atoms and those of the catalyst. Subsequently, the latter bonds are broken and electrons are relieved and the charged fuel ion combines with the electrolyte ion to form a product. The activation energy is required to permit these reactions to occur. The voltage drop due to activation polarization is expressed by an empirical equation, called the Tafel equation (Moore,1962; Austin,1960).

$$\Delta V_{chem} = a + b \ln J \qquad ....(16)$$

where J is the current density at the electrode; a and b are given by

$$a = b \ln J_o \qquad ....(17)$$

and

$$b = - \frac{RT}{\alpha nF} \qquad ....(18)$$

The quantities α and J_o are kinetic parameters. To reduce activation or chemical polarization, the gas diffusion electrode has been developed. The purpose of the gas diffusion electrode is simply to maximize the three phase interface of gas-electrode-electrolyte. It is, therefore, an electronic conductor with many small pores in it ranging from 10 to 100 microns in diameter. The pores create large reactive surface areas per unit geometrical area and allow free flow of reactants and products. The removal of products such as water in a H_2/O_2 fuel cell is crucial in order to prevent drowning of the electrode, which precludes further reaction.

The activation or chemical polarization can be minimized by an effective electro-catalyst and by increasing operating pressure and temperature.

4.2 Concentration Polarization:

As the reactants near the electrodes are rapidly removed by the electrochemical reactions, more reactants have to diffuse to the electrode from the bulk of the electrolyte in order to maintain the reaction. A concentration gradient is set up in the electrolyte which produces a back emf which opposes the voltage that a fuel cell would deliver under completely reversible conditions. At the anode, where ions are being discharged from the electrode into the electrolyte and a concentration buildup occur, the concentration potential is given by (Angrist,1982).

$$\Delta V_{conc(a)} = \frac{RT}{nF} \ln \left[\frac{J_L + J}{J_L} \right] \quad ....(19)$$

where J is the current density and J_L is the maximum current density, which occurs when the electrolyte near the electrode is completely depleted. For a consumptive electrode process such as at the cathode, where ions are being removed from the electrolyte, the concentration potential is given by

$$\Delta V_{conc(c)} = \frac{RT}{nF} \ln \left[\frac{J_L}{J_L - J} \right] \quad ....(20)$$

It should be noted that $\Delta V_{conc(a)}$ is usually small as the logarithmic term in equation (19) can never exceed ln2 as J approaches J_L. The concentration polarization can be reduced most effectively by the vigorous stirring of electrolyte and by increasing the operating temperature which tend to accelerate ionic diffusion within the fuel cell. Tobias et al (1952) and Eisenberg (1962) have discussed by analytical methods for predicting the effect of forced convection of the electrolyte on the limiting current that can be drawn from a cell.

The last type of concentration polarization is that due to changes in concentration of the reactant gases in the immediate vicinity of the reaction zone at the electrode. The gas pressure in the pores of the electrode must be sufficiently large to prevent the drowning of the electrode by the electrolyte. That is, it must be able to maintain three phase equilibrium within the pores of the electrode. The difference in pressure between the gas supply and the pressure found at the reaction zone causes a reduction in potential similar to the concentration gradient in the electrolyte.

$$\Delta V_{conc(g)} = \frac{RT}{nF} \ln\left[\frac{p_r}{p_g}\right] \qquad ....(21)$$

where p_r is gas pressure in the pores and p_g is bulk gas pressure. In general, this loss is small and can be neglected if pure reactant gases are used. However, for a gas mixture gas concentration polarization may be significant. For example, if the oxidizer is air then p_g must be the partial pressure of the oxygen in the air while the electrolyte might be at the pressure of the air.

4.3 Resistance Polarization:

During an electrochemical reaction at an electrode, there is generally a significant change in the specific conductivity of the electrolyte, which involves an additional loss of potential. Electrical resistance in the electrodes and conductors leading to the cell terminals is also of some significance, since fuel cells are a low-voltage device and high currents have to be conducted.

4.4 Heat Transfer in Fuel Cell:

The heat released within a fuel cell comes from three distinct effects taking place in the cell:

(i) The electrochemical reaction that gives rise to the reversible heat transfer;

(ii) The fuel reacting chemically with the oxidiser rather than electrochemically to generate an irreversible heat transfer;

(iii) The cell operates at some voltage less than the theoretical open circuit voltage with the difference manifesting itself as I^2R or $I\Delta V$ heat in the cell, where I is the current drawn, R and ΔV represent irreversible resistances and voltage drops respectively.

The reversible heat transfer is obtained only from those moles of fuel that react electrochemically to produce an electric current, namely $\eta_f N_{fu}$. Thus, the reversible heat transfer rate is

$$
\begin{aligned}
Q_{rev} &= \eta_f N_{fu} \ (T\Delta S) \\
&= \eta_f N_{fu} \ (\Delta H - \Delta G) \\
&= \frac{I}{nF} \ (\Delta H - \Delta G) \qquad \ldots\ldots\ldots(22)
\end{aligned}
$$

where, $\eta_f N_{fu}$ has been eliminated in favour of the current by use of equation (14). Since $T\Delta S$ for most reactions of interest (see Table 1) is negative, the reversible heat transfer in most cases will be away from the cell.

The part $(1-\eta_f)$ of the fuel supplied that reacts chemically, but not electrochemically, with the oxidant is also turned into heat. This amounts to

$$
\begin{aligned}
Q_{chem(irr)} &= (1-\eta_f) N_{fu} (\Delta H) \\
&= \frac{I}{nF} \ \frac{1-\eta_f}{\eta_f} \ (\Delta H) \qquad \ldots\ldots\ldots(23)
\end{aligned}
$$

Since ΔH is negative for most reactions of interest (see Table 1), this results in heat transfer away from the cell.

Finally, the heat transfer also takes place because of the irreversible voltage drop that occur in the fuel cell. As discussed earlier, the cell operating voltage is below the theoretical open circuit voltage due to activation and concentration polarization at each electrode as well as I^2R type voltage drop occuring in each electrode and in the electrolyte. Considering the fuel that reacts electrochemically to produce an electrical current

$$Q_{\Delta V} = \eta_f N_{fu}(nF)(V_{ac}-V^o)$$

$$= I(V_{ac}-V^o) \qquad ....(24)$$

The total heat transfer is then

$$Q_t = Q_{rev} + Q_{chem(irr)} + Q_{\Delta v}$$

$$= \frac{I}{nF}(T\Delta S) + \frac{1-\eta_f}{\eta_f}(\Delta H) + nF(V_{ac}-V^o) ...(25)$$

The second term will generally be small, since η_f is usually close to one.

5.0 FUEL CELL TYPES

In the course of more than 140 years of development, various types of fuel cells have evolved. Some are at a rather advanced stage, others are still little more than laboratory curiosities. Fuel cells can be classified according to a number of different configurations, depending on the combination of type of fuel and oxidant, whether the fueling is direct or indirect, the types of electrolyte and the temperature of operation. The fuel cell parameters are listed in the Table 3. In a direct fuel cell, the fuel used is readily oxidised electrochemically and is fed directly. In the indirect system, the fuel is first converted in a fuel processing subsystem to an easily oxidized hydrogen rich gas, which is then fed into the fuel cell.

Fuel cells can be classified by coupling the electrolyte systen with temperature based upon the electrolyte's thermal capability as follows:

Low temperature (<260°C):
- Alkaline fuel cell (65°C - 160°C)
- Solid polymer electrlyte fuel cell (<120°C)
- Phosphoric acid fuel cell (175°c - 200°C)

High temperature: (600°C - 700°C)	Molten carbonate fuel cell
Very high temperature: (>750°C)	Solid oxide fuel cell

Table 3: Fuel Cell Parameters

Fuel		Oxidant	Temperature °C	Electrolyte
Direct	Indirect			
Hydrogen	Hydride	Oxygen	Low(<260)	Aqueous Acid: Sulphuric Acid
Hydrazine	Ammonia	Air	High (600-700)	
Ammonia	Hydrocarbon	Hydrogen-peroxide	V.High (>750)	Phosphoric Acid
Hydrocarbon	Methanol			Aqueous Alkaline: Sodium Hydroxide, Potassium Hydroxide
Methanol	Ethanol			
Coal Gas	Coal Gas			
Coal	Coal			Solid Polymer Electrolyte
				Molten Carbonate
				Solid Oxide

Source: Linden, 1984

The cells that have been most extensively developed are those that use hydrogen as their fuel and oxygen or oxygen in air as the oxidant. Figure:5 plots cell voltage, a measure of efficiency, against cell

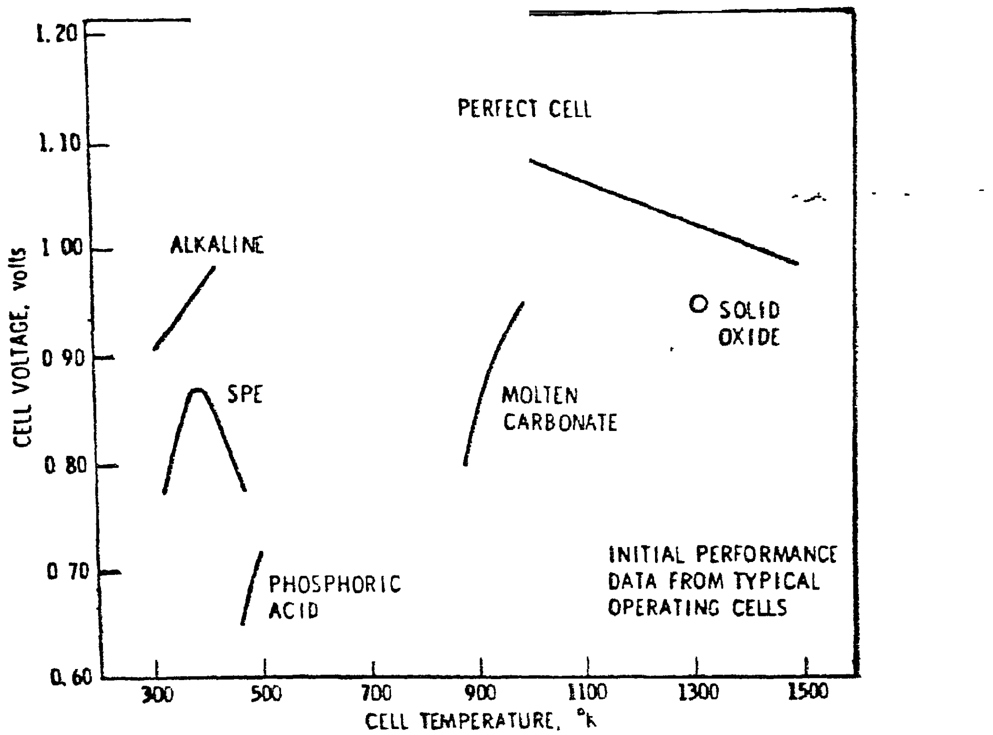


Figure 5 : Cell Voltage vs. operating temperature for different fuel cell types ([illegible], 1981)

operating temperature for all fuel cell types that are currently under development. A perfectly efficient fuel cell is shown for comparison. Even though phosphoric acid cell has the lowest efficiency of the fuel cell types shown, it is technologically most advanced. It is considered as the first generation fuel cell and has the best combination of proven cell life, tolerance to impurities in the fuel and oxidant and low cost. Molten carbonate fuel cell is considered as the next generation fuel cell, while solid oxide fuel cells are being developed for the long term. Alkaline and solid polymer electrolyte fuel cells are intended mainly for vehicular applications. Not much work has been done on alkaline fuel cells while solid polymer electrolyte fuel cells are in experimental stage.

5.1 Low Temperature Fuel Cells

5.1.1 Alkaline Fuel Cells:

They are modification of the Bacon's H_2/O_2 fuel cell. Although early alkaline fuel cells operated at relatively high temperature (~ 250°C) with concentrated (85 wt %) potassium hydroxide. Systems developed more recently (Angrist,1982) operate at much lower temperatures (~120°C) using less concentrated (35 to 50 wt %) potassium hydroxide. The lower temperature enables the use of matrices to retain the electrolyte and increases the life of other components. In the alkaline fuel cell, ionic conduction through the electrolyte is provided by hydroxyl (OH^-) ions.

A wide range of electrocatalysts are used including nickel, silver, metal oxides and noble metals. These cells in various modifications, e.g. involving combination of the Bacon's porous nickel electrode structure with a polytetrafluoroethylene (PTFE) bonded active carbon layer on the gas side have demonstrated long term reliability in applications where pure hydrogen and oxygen are used. Allis-Chalmers have successfully developed three basic building block fuel cell modules for space use. Their cells include a radiation-cooled 200 watt module; a gas or liquid cooled 2 kW module and a liquid cooled 5 kW module. Each of these fuel cell modules employs a capillary matrix electrode-electrolyte concept. Water management and heat transfer are intimately related; often evaporation of water consumes about one-third of the heat to be rejected. The static moisture removal system developed for space craft provides an interesting example of how this problem can be solved. In each cell the potassium hydroxide (KOH) electrolyte is immobilized in an asbestos matrix. The porous electrodes are held firmly against the faces of the matrix. A second matrix, also containing electrolyte (KOH) and supported on both sides by porous nickel plaques, forms a wall between the anodes chamber and a space called the moisture-removal cavity. Water evaporates from the fuel cell electrolyte, diffuses as vapour to the second matrix, diffuses as a liquid through this matrix and finally evaporates into the moisture-removal cavity. The driving force for this transport process is the chemical potential of water as measured by its vapour pressure and this driving force is controlled by a temperature compensated electronic controller which vents water vapour to vacuum when the vapour pressure in the cavity exceeds the desired value. Figure:6 is a schematic of what is taking place in the cell. The 2 kW system is a typical of fuel cell space power systems. The fuel cell stack used in this module consists of 32 series connected cell sections, with each section consisting of two parallel connected cells.

A major obstacle to commercial application of alkaline fuel cell is the need to remove carbon dioxide (CO_2), since it reacts with hydroxide ion to give the considerably less conducting bicarbonate ion:

$$OH^- + CO_2 \text{ ----> } HCO_3^- \qquad ....(26)$$

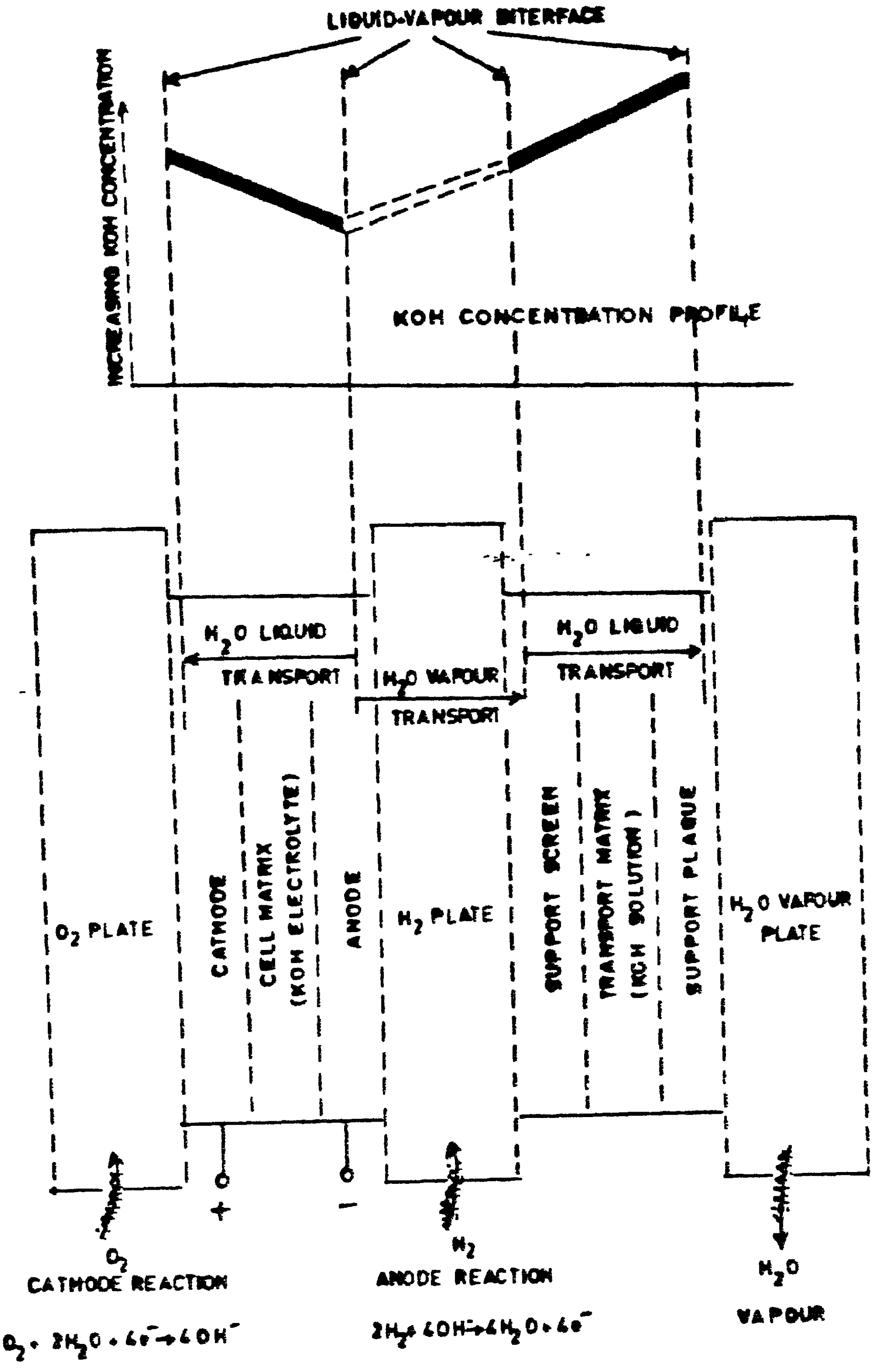


Figure 6 : Schematic of Water transport in the Allis Chalmers Fuel Cell. (Angrist, 1982)

This severely limits the cell's performance. Thus, alkaline fuel cells have only limited application where carbonaceous fuels or air are used as reactants. The important applications of these cells (space and undersea) both use pure hydrogen and oxygen.

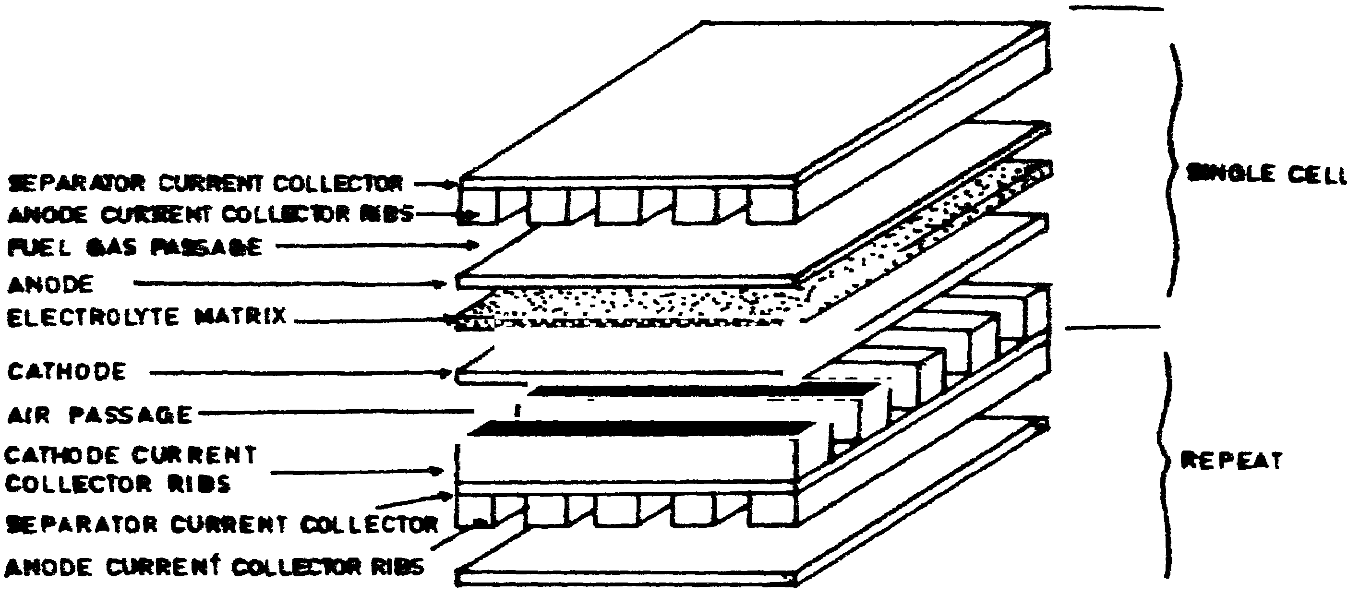
5.1.2 Acid Fuel Cells:

The type that has remained most similar to the original fuel cell of Grove (Liebhafsky,1968)is the acid fuel cell. Many acid electrolytes have been considered for use in these fuel cells which tolerate carbonaceous fuel as well as CO_2 in the oxidant gas. Among the acids commonly available, hydrochloric acid is rejected (Mc Dougall,1976) as it easily loses hydrogen chloride gas when other gases are bubbled through it or come into contact with it in the electrode pores. Nitric acid has too great an oxidising power and consequently is very damaging to the cell structure and the electrodes. Other acids are either too little dissociated (e.g. acetic acid) or too expensive (e.g. hydroiodic acid). Sulphuric acid may be used as an electrolyte due to its higher conductivity. However, it is highly corrosive, viscous when concentrated and has a high heat of dilution. It has considerable oxidising power and may yield hydrogen sulphide, a serious catalyst poison, on reduction. Phosphoric acid, despite its comparatively low dissociation constant, is currently most prominent electrolyte. Besides the aqueous acid electrolytes, solid polymer electrolyte (which are also acidic in nature) have been used.

(a) **Phosphoric acid fuel cell:**

Phosphoric acid fuel cell (PAFC) is technologically most advanced and for a number of years it has been the leading candidate for terrestrial applications. It is aimed at both Multikilowatts onsite integrated energy system as well as Multimegawatts utility electric generation. Three major teams have worked on improving cell performance namely, UTC, Westinghouse Electric Corporation and ERC. Their efforts have been summarised by Simons et al. (Simons, 1981).The phosphoric acid electrolyte system operates at 150°-200°C. At lower temperatures, phosphoric acid is a poor ionic conductor, at high temperatures, material stability (carbon and platinum) becomes limiting. The basic cell structure (as shown in Figure:7) (Linden, 1984) consists of:

(i) Carbon or graphite separator - current collector plate that separates hydrogen from the air to the adjacent cell (in a multicell stack) and also provides the electrical series connection between the cells.


SEPARATOR CURRENT COLLECTOR
ANODE CURRENT COLLECTOR RIBS
FUEL GAS PASSAGE
ANODE
ELECTROLYTE MATRIX
CATHODE
AIR PASSAGE
CATHODE CURRENT COLLECTOR RIBS
SEPARATOR CURRENT COLLECTOR
ANODE CURRENT COLLECTOR RIBS
SINGLE CELL
REPEAT

(ii) Carbon or graphite anode current collector ribs that conduct the electrons from the anode to the separator plate and also provides passage of fuel to anode.

(iii) An anode that consists of a porous graphitic substrate with the surface adjacent to the electrolyte treated with expensive platinum catalyst (0.25 mg/cm^2). Teflon is usually employed as a catalyst binder.

(iv) An electrolyte matrix that retains 90-100 % phosphoric acid.

(v) A cathode is similar to the anode but uses a modified noble metal catalyst and an increased catalyst loading (0.5 mg/cm^2), it is also made hydrophobic by increasing the Teflon content.

(vi) Cathode current collector ribs that are also virtually identical to the anode ribs.

These single cells are stacked in series to produce the desired output power. Fuel, air supply and exhaust manifolds are then connected along the respective sides of the stacks. Cell seals are located between the separator plate and electrolyte matrix to prevent overboard leakage of fuel or air. The manifold seals are located between the respective sides of the stack and the manifolds. The cell sealing is usually accomplished by a "wet seal", i.e. the surface tension of the phosphoric acid wetting the component surfaces is sufficient to provide sealing. The manifold seal is accomplished with a Teflon type of caulking. To mitigate sealing difficulties during operation at high pressure, the stacks are housed in a pressure container, which allows the container to be pressurized to operating pressure and minimizes the differential pressure across the seals. Hydrogen rich gases, such as those derived by reforming of hydrocarbon serve as the fuel, air or pure oxygen serves as the oxidants.

The electrochemical reaction is:

$H_{2(g)} \longrightarrow 2H^+ + 2e^-$ Anode ....(27)

$2H^+ + 1/2O_{2(g)} + 2e^- \longrightarrow H_2O_{(g)}$ Cathode ....(28)

$H_{2(g)} + 1/2O_{2(g)} \longrightarrow H_2O_{(g)} + \text{electricity}$ Net

The advantages of phosphoric acid fuel cells are:

(1) The electrolyte is very stable.

(2) The phosphoric acid can be highly concentrated.

Single cells operate at 175°C and attained 160 mA/cm^2 at 0.64V (Selman,1981) (38% efficiency.) The 40 kW unit operates at ambient pressure, 190°C to 200°C and between 100 and 200 mA/cm^2 (Linden,1984). UTC's cell stacks in the Edison demonstration plant contains 20 stacks, each having 500 cells of 3400 cm^2 area each. It operates at 3.4 atm. and 190°C. Average cell voltage is just over 0.65 V initially, dropping to about 0.62 - 0.63 V after 4,000 h. So far, UTC has run successful tests of these cells upto 25,000 hours (almost 3 years). Newer cells of the same size, but operated at 8 atm. and 207°C produced an initial voltage of 0.75V, dropping to about 0.71V after 4,000 hours (Parkinson,1983).

The main goal for phosphoric acid fuel cells in the near future is to bring down the cost of power generation which is now (i.e. January 1983) is of the order of $ 4000/kW as compared to $ 1450 - $ 1700/kW for a coal-fired power plant (Parkinson,1983). This is expected to be achieved in two ways, by increasing the cell operating temperature, thus lowering capital cost by producing the same amount of electricity from a smaller cell; and by commercial volume production which will reduce manufacturing cost. Increased temperature speeds up corrosion, this is because acid concentration drops, and water attacks the graphite of which the cell structure is made. Or else, other electrolytes which are stable at high temperature could be used.

Besides, there are certain other problems with PAFC :

(i) PAFC cannot tolerate high carbon monoxide concentration, at the best one to two percent of carbon monoxide in the fuel; at low temperature chemisorbed CO is not oxidised fast enough which results in a partial passivation of the anode to H_2 oxidation.

(ii) The processes which have contributed to the decay in performance of electrodes used in PAFC are the loss of catalytic surface area, corrosion of carbon support, electrode structure degradation and impurities in the reactant stream.

(b) Solid Polymer Electrolyte Fuel Cell:

The solid polymer electrolyte fuel cell, developed by General Electric Company of USA, was the first fuel cell technology known to be used operationally. These 1kW units provided the onboard electrical power for Gemini spacecrafts during 1963-65 (Nuttal,1983). SPE fuel cells were also subsequently used on NASA's Biosatellite spacecraft and development programmes have covered a range of applications which include advanced space power systems, portable ground power and undersea power systems. The major current activity is the development of a space regenerative fuel cell system for energy storage board space stations and also for vehicular applications using methanol as the fuel.

SPE fuel cells are unique in that there is no liquid electrolyte to present problems of leakage or corrosion. The electrolyte used is a solid sheet of plastic similar to Teflon which is sulphonated to give it the capability to conduct hydrogen ions (ion exchange membrane). Being a solid material, it provides a rugged barrier between the hydrogen and oxygen reactant gases, while providing a thin electrical efficiency. The electrode structures are merely thin films of catalyst pressed on to the electrode surface. For the fuel cell cathode, a thin wet proofing film is placed over the electrode in order to prevent product water from obstructing the active surface. Cells of this type have been life tested for more than 60,000 hours with minimal performance degradation. The advantages of the SPE fuel cell are:

(1) The electrolyte, being a solid cannot change, move about or vapourize from the system.

(2) The only liquid in the fuel cell is water which minimizes corrosion.

The disadvantages are:

(1) The SPE must be hydrated (water saturated) to perform; consequently, operation must be under conditions where the byproduct water does not vapourize

into the reaction air stream faster than it is produced; this constrains cell operation to under 60°C at ambient pressure and about 120°C at elevated pressures.

(2) The SPE freezes at about 0°C and undergoes a freeze drying phenomenon. This constrains applications to those where low temperature capability is not required.

Due to their inability to operate much above 120°C, SPE fuel cells are best suited for use with H_2-rich gases that contain little or no CO. Carbonmonoxide inhibits the fuel cell anode reaction. The degree of inhibition decreases with increasing temperature. Consequently, SPE fuel cells have found their important applications in the space programme operating on pure hydrogen or in military applications. Approaches are being evaluated that would allow future SPE cells to operate with fuel gases containing CO. These techniques involve improving the anode, electrocatalysts and prehumidifying the air, to allow the operating temperature to be increased.

5.2 High Temperature Fuel Cells:

These cells operate at temperatures between 600°C - 700°C. The main incentive for increasing the temperature was the expectation that favourable electrode kinetics at high temperature will permit the use of inexpensive catalyst material. Also it has been assumed that fossil fuels can be reacted directly at high temperature. Acid electrolyte has not been considered for these cells because the increased temperature are likely to to cause severe corrosion effects. Therefore, there was a need to search for other suitable electrolyte which can work at high temperature. Thus one of the electrolytes which was found suitable was molten salt electrolyte.

5.2.1 Molten Carbonate Fuel Cell:

The processes occuring in a H_2/O_2 fuel cell operating at higher temperatures without an aqueous electrolyte might be contemplated as oxide ion produced at the oxygen electrode (McDougall,1976).

$$O_2 + 4e^- \text{---->} 2O^{2-} \qquad \text{.......(29)}$$

which then move to the fuel electrode to oxidise the hydrogen

$$H_2 + O^{2-} \text{---->} H_2O + 2e^- \qquad \text{.......(30)}$$

and it might therefore be considered that a molten ionic oxide would provide the best electrolyte to encourage this process. However, simple ionic oxides have melting points greater than 1000°C and therefore, attention was focussed on salts melting at lower temperature. These salts were generally those with O_2 containing anions e.g.nitrates, sulphates and carbonates. Since CO_2 is the major product and it may well react with any molten salt containing anions other than carbonate, displacing the appropriate acid anhydride which may then attack the electrode material or be otherwise troublesome

$$\text{e.g. } CO_2 + SO_4^{2-} \longrightarrow CO_3^{2-} + SO_3 \quad ....(31)$$

Hence, it is most satisfactory to consider as electrolyte a molten carbonate or mixture of carbonates; a mixture of salts may have a considerable advantage since it will have a lower melting point than either component on its own. A convenient way of maintaining the carbonate composition of the electrolyte invariant is to remove CO_2 a gaseous product from the fuel electrode and transfer it to the oxidant electrode in the air or O_2 stream. Thus, for a fuel such as CO the overall electrode processes might be

$$O_2 + 2CO_2 + 4e^- \longrightarrow 2CO_3^{2-} \quad ....(32)$$

$$\text{and } CO + CO_3^{2-} \longrightarrow 2CO_2 + 2e^- \quad ....(33)$$

thus carbonate ion transfer within the electrolyte may be balanced by CO_2 transfer outside it. A similar mechanism is valid by using H_2 as the fuel.

$$H_2 + CO_3^{2-} \longrightarrow CO_2 + H_2O + 2e^- \quad ....(34)$$

Following are the advantages of molten carbonate fuel cell over phosphoric acid fuel cell (Borys,1979).

(1) Higher Efficiency: Waste heat is removed from the cell at higher temperature of ~ 650°C, integration of the fuel cell sub-system wth a bottoming sub-system (electric power generation) or heat recovery system (for cogeneration) or with coal gasifier is attractive and thus has higher overall efficiency of 50%.

(2) More Economic: Since it works at high temperature, reaction kinetics of electrode processes are rapid, thus eliminating the need for expensive catalyst material, it uses inexpensive nickel electrode.

(3) Fuel Flexibility: Carbon monoxide can be used as fuel here. While in phosphoric acid fuel cell, it poisons the electrodes thus decreasing the need for fuel processing and favours a greater range of options for the fuel source.

This type of fuel cell is being developed in the USA by UTC in collaboration with IGT. Since US Department of Energy has set up a goal to bring to commercial development MCFC power plant operating on coal, so in most of the development work, gasified coal is used as fuel. The fuel is a mixture of N_2, CO, H_2, CO_2, H_2O (obtained from the coal gasification) and trace constitutents which enter the cell parallel to the anode and react at the anode - electrolyte interface. MCFC structure is geometrically similar to PAFC but materials used are different, it consists of (Linden,1984) (Figure:8).

(i) Like PAFC a separator and current collector plate

(ii) An anode current collector, made of nickel,

(iii) An anode that consists of a porous nickel treated with a refractory oxide to reduce sintering. At 650°C temperature, no other catalyst is required,

(iv) An electrolyte system comprising a mixture of lithium-potassium carbonate and inert powder(presently a lithium aluminate). The mixture forms a paste when molten and freezes to form a "tile" when cooled.

(v) A cathode is similar to anode except that it uses nickel oxide (doped with lithium to impart electronic conductivity). Since hydrophobic agents like Teflon are unstable at 650°C, cathode flooding is prevented by careful attention to the pore size in the anode, electrolyte and cathode.

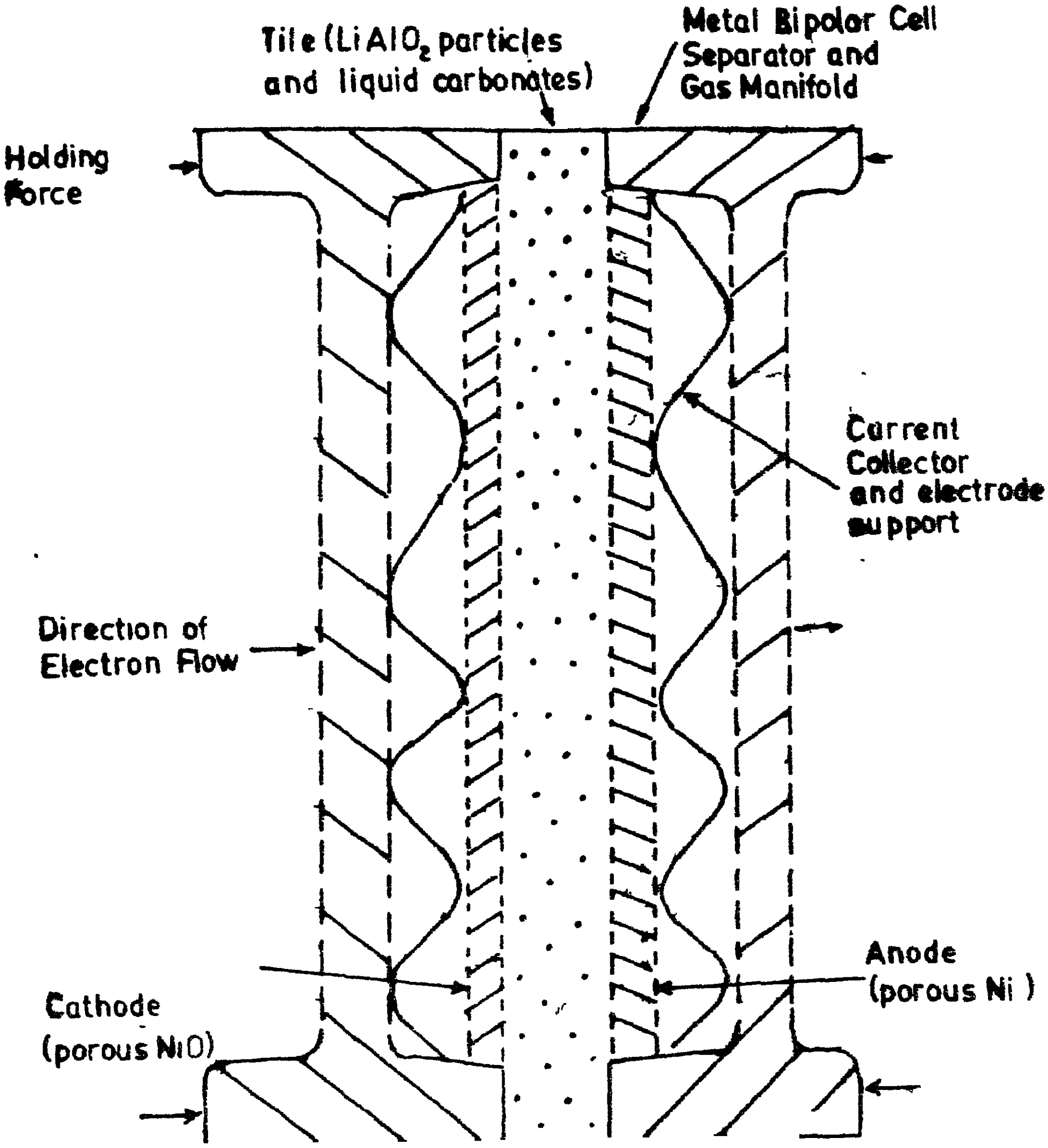

Tile (LiAlO₂ particles and liquid carbonates)
Metal Bipolar Cell Separator and Gas Manifold
Holding Force
Current Collector and electrode support
Direction of Electron Flow
Anode (porous Ni)
Cathode (porous NiO)

Figure 8 : Schematic of a molten carbonate fuel cell (Pierce, 1981)

(f) A cathode current collector that has similar requirements and configurational options as the anode current collector. Since nickel is thermodynamically unstable, material options include lithium doped nickel oxide and stainless steel. As with the PAFC individual cells are stacked in series to result in a stack cell and manifold sealing are accomplished by "wet seals" and the use of inert caulking. And when operating at pressure, the stacks will be contained in a pressure vessel.

Voltage output of a single cell is about 0.85 volt at 160 mA/cm^2 (Pierce,1981). Bench scale models have achieved lifetime in excess of 1500 hours (Angrist,1982). The largest test done so far is of 2kW (Parkinson,1983) cell stack by UTC in 1983. ERC hopes to capitalize on the cells characteristics by developing a direct molten carbonate cell that would process single carbon fuel directly by using the cell's heat to produce H_2 by steam reforming. The company has demonstrated a continuous operation of this type in the laboratory, using methane and methanol. The two applications of MCFC system that are being emphasized are large coal fired central station and industrial cogeneration. MCFC are in the Pilot plant stage. Major problems remained to be solved are:

1. CO_2 recycle from anode to cathode is necessary.

2. Electrolyte is lost by corrosion and vaporization in long term operation (> 40,000 h.).

3. Electrolyte and electrode undergo structural changes in long term operation. Control of these changes require much further effect.

The current emphasis of the DOE's MCFC programme is on development of stacks of cells. UTC and General Electric Co. are the major contractors in this programme.

5.3 Very High Temperature Fuel Cells

5.3.1 Solid Oxide Electrolyte Fuel Cell

There was need to search for an electrolyte which could satisfactorily work at still higher temperature i.e. 1000°C. In 1900, Nernst had conceived the idea that oxidic conductors could be used as light sources in lamps, in place of carbon filaments. He discovered that the low conductivity of pure zirconium oxide could be improved by adding other oxides. He found that $(Y_2O_3)_{0.15}(ZrO_2)_{0.85}$ was the most promising composition in this respect (Feduska,1983). When CaO or Yttria are mixed with the zirconia, some Ca^{2+} ions or Y^{3+} ions displace Zr^{4+} ions from their position in the lattice.

Because of the different charges on the replacing ions, this process leads to a certain number of oxide ions lattice sites becoming empty. At high temperature, it is possible for oxide ion to migrate through lattice via these vacant sites and hence the structure conduct electricity by ionic mechanism (M^cDougall,1976). Baur and Preis were the first to use a solid oxide as the electrolyte in a fuel cell operating at temperature >1000°C. Coke was used as the anode, the electrolyte was zirconia stabilised with Yttria or magnesia. Only partial oxidation of the carbon occured, resulting in a low fuel cell efficiency and current outputs of <1mA/cm^2. Later, single cell work by Weisbart and Ruka (Weisbart,1963) with calcia stabilized zirconia $[(ZrO_2)_{0.85}(CaO)_{0.15}]$ demonstrated that current densities well above 100 mA/cm^2 could be achieved with oxygen and hydrogen fuel. The pioneering work for the development of solid electrolyte cells stacks has been mainly at two research laboratories : Westinghouse Research and Development Centre (Isenberg,1977; Archer,1965; Ruka,1976) Brown Boveri and Cie (BBC), Germany (Rohr,1978). Development efforts began on it in 1962 and continued without interruption to 1970. The objective of this work was to develop a commercial fuel cell power generating system which use coal as fuel source.

The operating principle of SOFC is as follows (Isaacs,1981): Oxygen molecules in the air migrate down the pores in the cathode and react with electrons from the electronically conducting electrode material and enter an oxygen vacancy (V^{o++}) in the electrolyte, according to the reaction:

$$O_2 + 4e^- + 2V^{o++} = O_o \qquad ....(35)$$

Oxygen vacancies are formed at the anode by the extraction of an oxygen atom from an oxygen site (O_o) in the electrolyte lattice. The oxygen combines with either hydrogen or carbon monoxide in the fuel and liberates two electrons to the electrode i.e.

$$O_o + H_2 = V^{o++} + 2e^- + H_2O \qquad ....(36)$$

$$O_o + CO = V^{o++} + 2e^- + CO_2 \qquad ....(37)$$

the water or carbon dioxide formed diffuses down pores in the cathode to enter the fuel stream. This flow is opposite to the flow of the reactants H_2 and CO.The electrons produced flow to an external load.

Solid oxide fuel cells offer advantages similar to those of molten carbonate cells. Apart from these advantages they are believed to have several advantages over the PAFC and MCFC (Isaacs,1981; Srinivasan,1979).

1. No need to recycle the CO_2 stream from anode to cathode
2. Both PAFC and MCFC suffer from the problem of cell corrosion which does not occur in SOFC
3. Stable electrolyte
4. Since there are no liquids involved, hence none of the problems associated with pore flooding and maintenance of three phase zones
5. The ionic concentration of electrolyte is invariant and independent of the fuel and oxidant stream.
6. The system is noted to be sulfur tolerant so coal containing significant amounts of sulfur is expected to yield satisfactory performance with low parasitic losses.

Out of the three fuel cells (PAFC, MCFC, SOFC), currently under development in the U.S., SOFC integrated with coal gasifiers are projected to have the highest overall efficiency. They operate at 1000°C temperature. SOFC employ a "tubular" rather than "plate and frame" stack assembly of previous technologies (Figure:9). The tubular stack avoids the problem of sealing the edges. Such seals are considered impractical due to the lack of nonporous, insulating, gasket materials for use

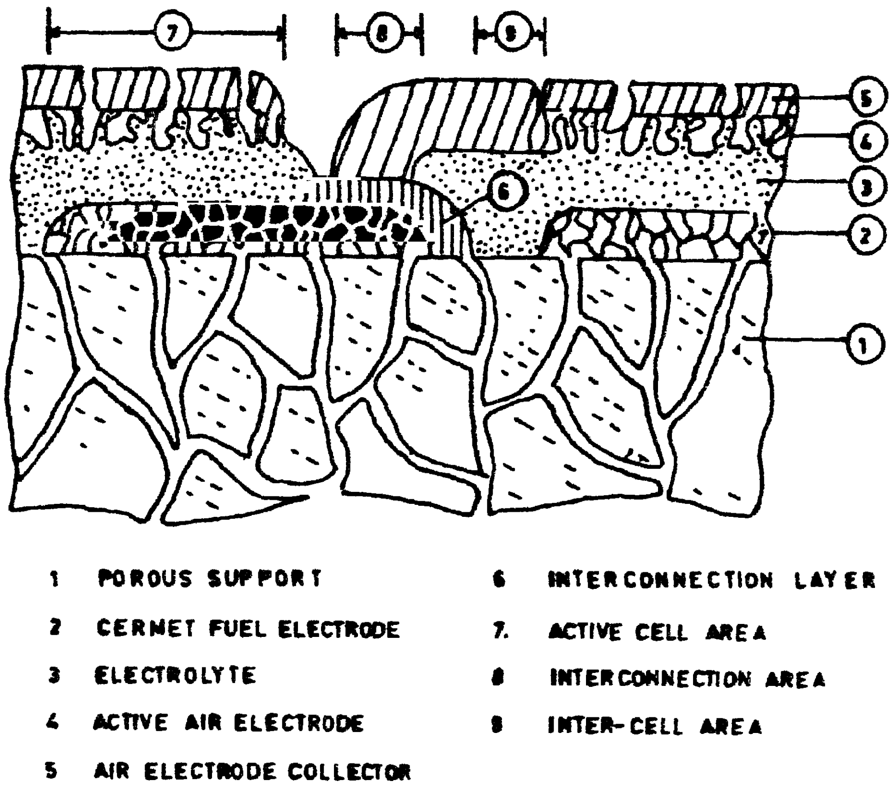


Figure 9 : Solid oxide electrolyte fuel cell stack (Isaacs, 1981)

at 1000^{o}C. The state of the art of solid oxide fuel cell consist of five basic components: a porous support tube, a fuel electrode, a solid electrolyte, an air electrode, and an electronically conducting interconnection.

(a) The porous support tubes are required to provide mechanically strong structure and also allow access of the fuel gas to fuel electrode and is made of calcia stabilized zirconia.

(b) The fuel electrode must be electronically conductive and must catalyze the fuel oxidation reaction, it is made up of porous nickel zirconia cermet.

(c) The electrolyte is a dense film of yttria stabilized zirconia.

(d) The air electrode is made of tin doped indium oxide and doped lanthanum manganite. To enhance performance, a catalyst such as praseodymium oxide can be incorporated into the electrode-electrolyte interface. The interconnection between cells in a stack is made of modified lanthanum chromite.

BBC have operated a single cell for over 50,000h and a multicell stack for over 10,000h (Isaacs,1981). A Westinghouse multicell stack (upto 20 cells) was designed, fabricated and tested for over 700h. The operating cell characteristics (200 mA/cm^2 at 0.7V) are encouraging with respect to meeting power plant performance goals (Isaacs,1981). SOFC are in the experimental stage. The primary disadvantages are the very high temperature of operation and the severe material constraints imposed by the high temperature.

6.0 INTEGRATED FUEL CELL SYSTEM

A general fuel cell system consists of several subsystems : fuel cell sub system, fuel processor, power conditioner and thermal management sub system as shown in Figure:10.

The main component of a fuel cell power plant is the fuel cell sub sustem which brings about the actual energy conversion of the fuel by electrochemical reaction. It consists of a plurality of single cells assembled in a stack, accessories for distributing fuel and oxidant and also for heat removal from the stack to maintain a steady operation temperature.

Hydrogen is the primary fuel for the fuel cells. Combustion of H_2 results in liberation of energy.

$$H_2 + {}^{1}/_{2}\, O_2 \text{ ----> } H_2O + \text{energy} \ldots\ldots.(38)$$

Pure hydrogen is very expensive. Following are other sources from which H_2 can be obtained.

1. Metal hydrides : They are attractive because they can store large amount of hydrogen more conveniently and with a higher energy density e.g. non reversible solid hydride like CaH_2

$$CaH_2 + 2H_2O \text{ ----> } Ca(OH)_2 + 2H_2 \quad \ldots\ldots.(39)$$

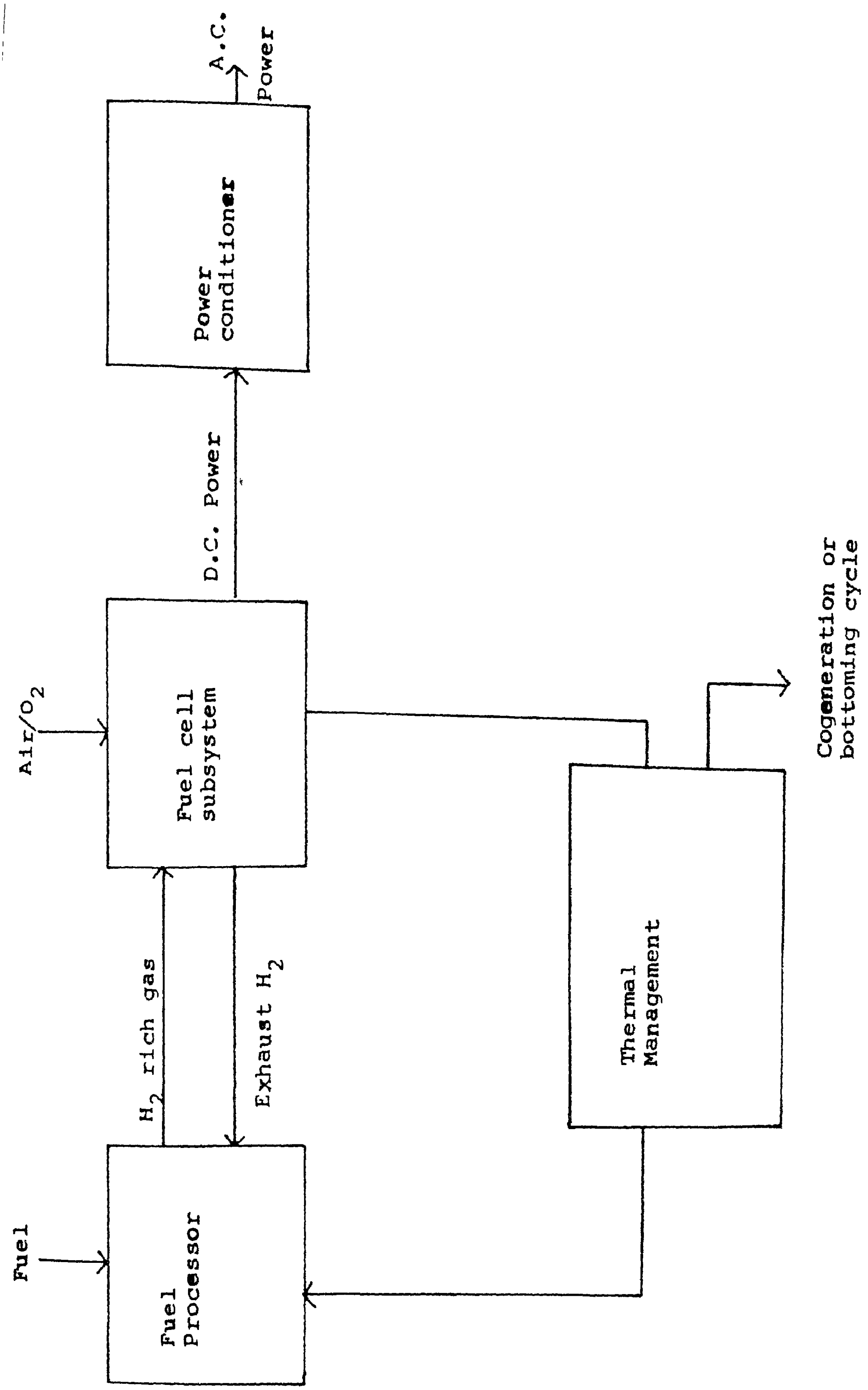


Figure 10: Schematic of Integrated Fuel Cell System

A second type of reversible hydride is based on the principle that certain metals or alloys (iron, titanium, lanthanum, nickel) have the ability to take up large amounts of H_2 gas with in their crystal structure. A decrease in pressure and increase in temperature release the H_2.

$$1.08FeTiH_{1.95} \longrightarrow 1.08FeTiH_{0.1} + H_2 \quad ....(40)$$

Other promising hydrides are $(LaNi_5)H_6$, $(FeTi)H_2$, $(Mg_2Ni)H_4$, the maximum hydrogen content being represented approximately by the formulas respectively.

2. Ammonia : Ammonia is decomposed catalytically into H_2 and N_2.

$$\underset{\text{(Anhydrous)}}{NH_3} \xrightarrow[\text{thermal cracking}]{750^oC} N_2 + 3H_2 \quad ....(41)$$

N_2 thus formed being inert, plays no role. It is most suitable for alkaline electrolyte since no CO_2 is formed here.

3. Hydrazine : N_2H_4 is injected into the electrolyte to provide the active material at the fuel electrode. (Suitable electrolyte is KOH).

4. Fossil fuels :

a) Natural gas (reforming) : It consists mainly of a mixture of simple paraffin hydrocarbon of which methane is by far the major constitutent (70-90 volume %), ethane (2.5 -7%), propane and butane (1-3%), and some higher paraffins are also present in decreasing proportion like (less than 1%), N_2 (less than 10%) (Glasstone,1983). Since methane is the major constitutent, it can undergo steam reforming to give H_2 and CO. Concentration of H_2 can be increased by water gas shift reaction.

Water gas shift reaction:

$$CO + \underset{(steam)}{H_2O} \dashrightarrow CO_2 + H_2 \qquad ....(42)$$

b) Coal : Coal on gasification give H_2, CO, CH_4. The actual heating value of coal gasification product depends on the proportion of these fuel constitutents and of the inert gases like N_2 (from air) and CO_2. These fuel gases are classified as high Btu, consists largely of methane. Intermediate Btu gas, consists of 65-70% CO and H_2 in various proportions, 5-15% CH_4 and remaining is CO_2. Intermediate Btu can be converted to high Btu by water gas shift reaction followed by methanation. Low Btu gas is more diluted with their inert N_2 gas.

c) Petroleum products: Among petroleum products, fuel oils are liquid mixture of hydrocarbons which are less volatile than gasoline.

5. Biomass : They are of interest because they represent a renewable source of energy. Fuel gases can be obtained from biomass by pyrolysis, or by biochemical conversion:

(i). Pyrolysis: Biomass (dry agricultural waste, wood, paper residues, municipal waste) on heating up to 90°C in absence of air is converted to combustible gas liquid (oils) and char. The gases are lower in sulphur content than coal gas and consist of CO, CH_4 and H_2 with CO_2 as the chief inert diluent.

(ii). Biochemical conversion: It is based on certain reactions occuring in the presence of enzymes, supplied by living microganisms. Two major biochemical processes have been worked out: (a) production of biogas from any form of biomass except wood, like animal and plant waste, algae, other organic substances with high moisture content. Biogas is 50 volume % of CH_4, remainder is CO_2 with small amounts of impurities. CO_2 can be removed to yield a gas with heating value of 37 MJ/Cu.m. (b) The fermentation of wood, starch and sugar gives alcohol, methanol and ethanol. Methanol is attractive for fuel cell use since it is more convenient to store, handle than either H_2 or NH_3 and can be easily reformed to H_2 than the long chain hydrocarbons (Glasstone,1983).

$$CH_3OH + H_2O \xrightarrow[200^\circ C,\ \text{catalyst}]{\text{steam reforming}} 3H_2 + CO_2 \quad ....(43)$$

It can react directly also:

$$CH_3OH + {}^3/{}_2O_2 \longrightarrow CO_2 + 2H_2O \quad ....(44)$$

Both ethanol and methanol can be chemically synthesized also.

Heating value of various fuels is given in Table 4.

Fuel is selected according to the end application of the fuel cell e.g. for space applications, or for transportation purposes (size range from few watts to 20 kW system), where light weight and small volume are important requirements. Fuels like methanol, ammonia, hydride and hydrazine are preferred over other fuels since they can be easily used by the system without the elaborate fuel processing system. For utility fuel cell power plants, cost and easy availability of fuels are the factors to be considered while selecting fuels. Here mainly fossil fuels are used, while fuels obtained from biomass are given a thought now. These fuels being

Table 4: Heating Values of Various Fuels

Hydrogen$_{(g)}$	12.1 MJ/cu.m.
Methane	38.3 MJ/cu.m
Carbon monoxide	12 MJ/cu.m
Fuel oils	38100-41500 MJ/cu.m
Methanol	16000 MJ/cu.m
Ethanol	21000 MJ/cu.m
Calcium hydride	22968 MJ/cu.m
Gasified coal:	
High Btu gas	35-39 MJ/cu.m
Intermediate Btu gas	11-17 MJ/cu.m
Low Btu gas	4.8-7.4 MJ/cu.m
Ammonia	13572 MJ/cu.m
Hydrazine hydrate	12816 MJ/cu.m

Compiled from Glasstone,1983 and Adlhart,1977.

complex cannot be used as feed for the fuel cells. They have to be converted to a H_2 rich stream which requires a fuel processor. It may comprise of one or more of the components depending on the fuel. Impurities from the fuel like sulphur and chlorides are removed before it enters the fuel converter, which may otherwise poison the catalyst used in fuel processor and also the fuel electrode of the fuel cell. Because water is required in the fuel conversion processes and is produced in the fuel cell reaction, the required water may be recovered from the exhaust gases. Depleted gases from the fuel cell may also be recycled to the fuel converter or burned to provide for the endo-thermic heat of reaction.

Power conditioner sub system efficiently converts DC power to AC, regulates output voltage and power, controls various sections of the fuel cell system and provides a safe operation. Thermal management sub-system is also dependent on the end application of the fuel cell e.g. no heat recovery is practiced in small systems, some process steam or space conditioning is obtained using the waste heat in on-site plants. Thermal management also depends on the kind of fuel cell used i.e. whether its PAFC , MCFC or SOFC. Because the waste heat in PAFC is not at very high temperature and may not be very useful as compared to the heat liberated in SOFC and MCFC which are respectively at temperatures of 1000°C and 650°C. Nevertheless, irrespective of the type of fuel cell, large power plants are designed with topping and/or bottoming cycles. So the waste heat recovery, therefore, can significantly improve the overall efficiency of the system. Currently among the integrated systems, 40 kW onsite plants and 4.5 MW units are being commercialised, their characteristics are listed in Tables 5 and 6 respectively.

Table 5: Characteristics of 40 kW On-site Power Plant

Modular size	~ 40 kW
Stack temperature / pressure	190^{o}C, 1x10^{5}Pa
Electrical efficiency (based on HHV)	39 %
Total efficiency (including heat recovery)	85 %
Fuel capability	All pipeline quality fuels
Design life	20 years
Noise	<60dbA at 3m.
Operation	Automatic
Output	3 phase,120/208V ac
Footprint	5 m^{2}
Available heat: at 80^{o}F	3.75 x J/kWhx10^{6}

Source: Linden, 1984.

Table 6: Characteristics of 4.5 MW Demonstrator Power Plant

Fuel	Natural gas, naphtha, SNG
Module size	4.5 MW
Heat rate (Btu/kWh) After 40,000 operating hours	
- full load	9300
- half load	9000
Projected life	20 years*
Projected cost ($/kW)**	~750
Efficiency (%) (cogeneration mode)	75 - 80

* Book life, with cell stack replacement every 40,000 h.

** In 1979 US Dollars, not including interest during construction and installation, assumes a production rate of 500 MW per year (Loftness, 1984).

Table 7: Comparison of Fuel Cell Power Plants with Various Electrolytes

System	Capital cost $/kW	Overall system efficiency (%)	Electricity cost (COE) mills/kWh	Projected lowest COE mills/kWh
Phosphoric acid	350-450	24-29	42-50	High 30
Alkaline	450-700	26-31	46-61	Low 40
Molten Carbonate	480-650	32-46	38-70	Low 30
Solid Electrolyte	420-950	26-53	35-61	High 20

Note: Based on 1974 US Dollors (Isaacs,1981)

7.0 ADVANTAGES OF FUEL CELL OVER THE CONVENTIONAL SOURCES OF POWER

1. (a) Direct conversion of the energy of the fuel into electric energy in fuel cells, avoids the heavy losses inseparable from the indirect conversion via heat and mechanical energy. Typical efficiencies are in the neighbourhood of 35% to 40% and vastly exceed those of other onsite generation system as given in Table 8, Figure:11. Increased efficiency could mean basic energy savings of 20% to 50% compared to standard thermal engines or traditional power stations (Leuckel,1976).

(b) They are not limited by Carnot cycle efficiency, so that heat rates as low as 7200 Btu/kWh can be projected. Current PAFC technology can provide heat rates of 9000 Btu/kWh. Advanced fuel cells are expected to deliver heat rates as low as 7014 to 7486 Btu/kWh, (Fickett,1978).

(c) Heat rate (or efficiency) is constant over a wide range of loads and independent of plant size.

(d) Fuel cells perform with high efficiency at part load also (Figure:12).

Table 8: Summary of Energy Conversion Devices

Device	Availability	System Efficiency	Application
Steam Turbines	Commercially available	35-41%	Predominantly fossil and nuclear central station-base load.
Internal Combustion Engines	Commercially available	35%	Small central station and peaking.
Gas Turbines	Commercially available as [a]ASUD	27-38%	Direct cycle for peaking. Topping cycle for fossil, central station.
Binary Cycles	ASUD	Up to 55%	Potassium topping cycle for fossil central station.
Fuel Cells	ASUD	Up to 70%	Central station or dispersed generation - energy storage features.
Batteries	ASUD	60% (turnaround)	Energy storage for load leveling and reliability.
Magnetohydrodynamics	ASUD	Up to 60%	Direct or topping cycle for central station.
Thermionic devices	ASUD	Up to 50%	Topping cycle on fossil or nuclear central station.
Thermoelectric devices	Suitable materials being sought	6%	Low power only.

[a]ASUD Advanced Systems Under Development (Loftness,1984).

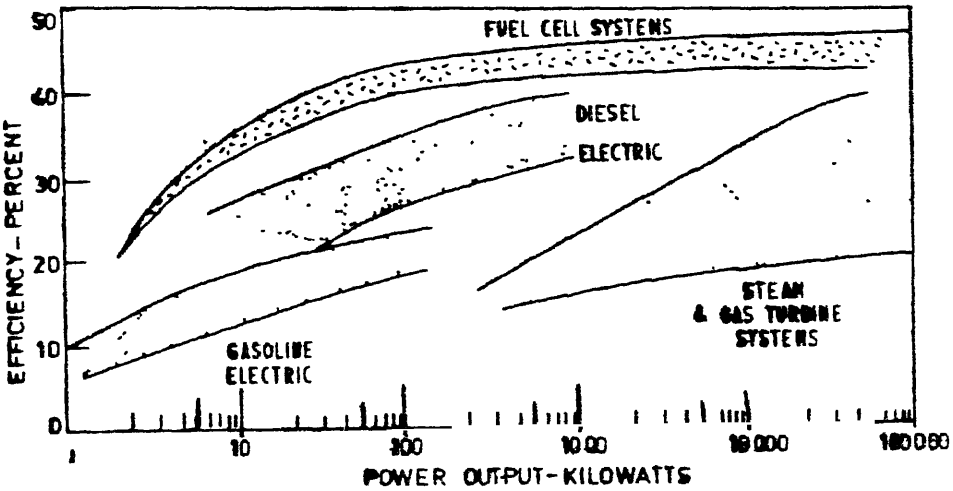


Figure 11 - Efficiency comparison of common modes
of on-site power generation
(Senarvi, 1980)

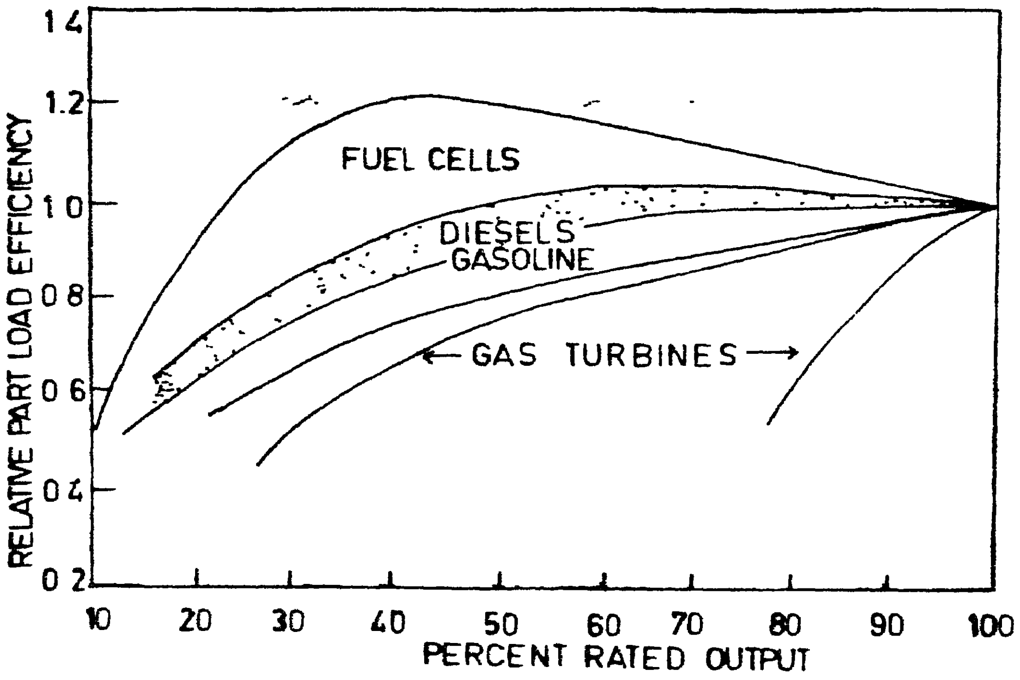


Figure 12 : Part load efficiency characteristics of fuel cells (Sanghvi, 1980.

(e) There is almost instant (millisecond) response to changes in power demand i.e. the fuel cell can go from part load to full power in less than one cycle.

Characteristics (d) and (e) are utilized in supplying utility systems Spinning Reserve requirements. Spinning reserve refers to power plants kept on line either at idle or part power to permit rapid system response to demand changes and to provide continuity of service in the event of a plant outage. In this type of operation, low part power heat rate and millisecond response to load change are important generator features. Combining conventional units at rated load with fuel cell units at part load could prove to be an efficient, economic mix. The use of fuel cells to provide spinning reserve capacity could permit up to 15% reduction in overall utility system fossil fuel consumption (Leuckel,1976).

2. It gives high power in unit volume, high power in unit weight; hence, they conserve capital.

3. Since the fuel cell essentially avoids combustion process they virtually cause no air pollution. A comparison of emissions from conventional power plants with those from an experimental fuel cell

operating on natural gas shows the measured emissions of NO_x, SO_2, smoke and particulates from the fuel cell are one-tenth to 1/50,000th of those of conventional electric generators (Table 9).

Table9: A Comparison of Emissions From Conventional Power Plants with those from an Experimental Fuel Cell Operating on Natural Gas

Pollutants	Federal Standards on Central Stations (lb/mil Btu)			Acid Fuel Cell Power Plant
	Gas-fired	Oil-fired	Coal-fired	
Air Particulates	0.1	0.1	0.1	0.0000029
NO_x	0.2	0.3	0.7	0.013 - 0.018
SO_2	No requirement	0.8	1.2	0.000023
Smoke	20% Opacity	20% Opacity	20% Opacity	Negligible

Source : Larson, 1980.

4. Heat produced in the electrochemical reaction of the fuel cell can be recovered with no reduction in generation efficiency and can be put to practical use. In this way more than 80% of the energy value of the fuel can be used in many applications (Figure:13) (Leuckel,1976).

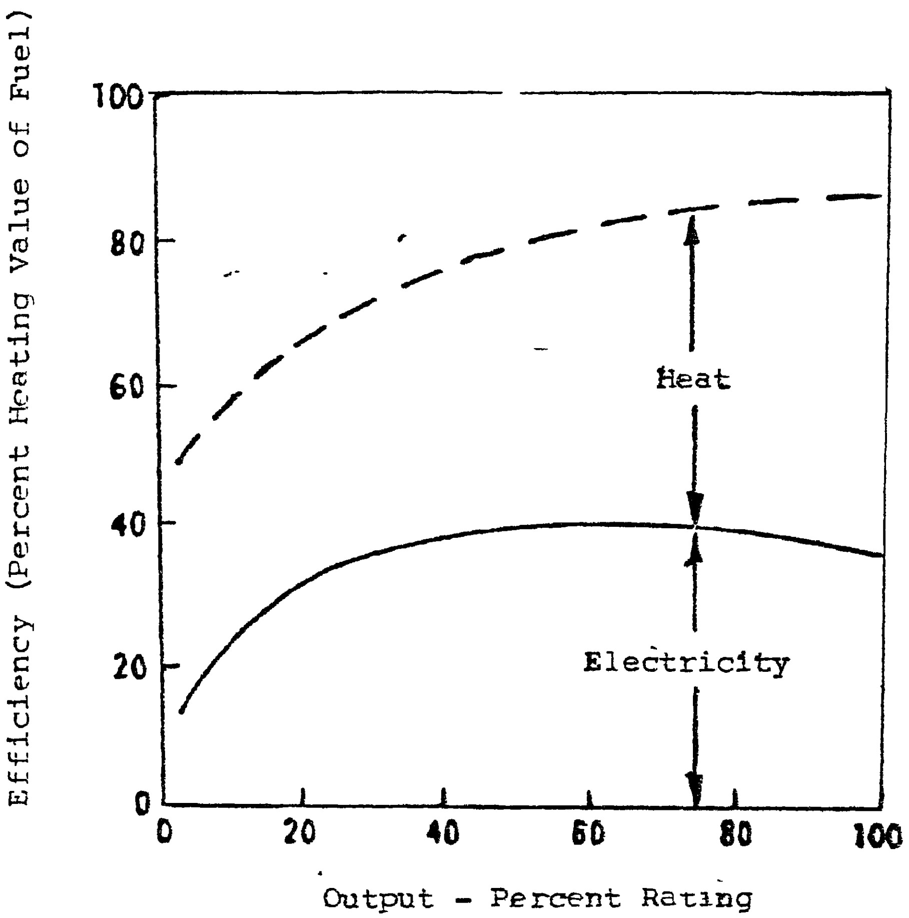


Figure 13: Total fuel cell efficiency (Leuckel, 1976)

5. Fuel cells are also small and modular, so they would be very attractive as onsite generators in both rural and urban areas. Since traditional electrification approach for widely dispersed rural population is undesirable, due to costly transmission line and also due to loss of energy (5-20%) in transmitting power from remote central plant. In urban areas e.g. multiunit residences and commercial establishment have been identified as economically attractive initial near term application for onsite power generation. Fuel resource savings of the order of 25-30% are readily achieved with such onsite fuel cell system. Besides, this waste heat recovered from the fuel cell could be used for spaceheating, hot water needs and industrial processes.

6. Another advantage is fuel flexibility. It can use natural gas, methanol, light petroleum distillates and medium Btu gas from coal gasification or other forms of synthetic fuels of the future. Accordingly, this technology will not become redundant if certain fuels become unavailable. It does not require large additional capital investment to switch from one fuel to another.

7. The fuel cells are quiet and clean in operation and are highly reliable.

8. The fuel cell process is continuous unlike the batteries. It works as long as the fuel and air are supplied and a load is connected.

9. Fuel cell power plants require no operating personnel except in the start up process which is also nearly automatic. Major parts will need to be replaced every five years and the life of the power plant is expected to be around 20 years. So the fuel cells have low maintenance requirements.

10. Process water supply is not needed since fuel cell by product, water, is used in the fuel conditioner.

These qualities are of importance with regard to the present preoccupation with saving of energy reserves and the concern for protection of the environment.

8.0 STATUS OF FUEL CELL RESEARCH AND POTENTIAL APPLICATIONS IN INDIA

Energy consumption is an index of a countrys economic development. It has been estimated that if the economic growth rates in India were to be in the range of 5.5-6%, the energy requirements in India would register a four-fold increase within the next 20 years There has been a steady increase in the share of consumption of the commercial forms of energy (coal, oil, gas and electricity) from about 32% in 1952 to 64% in 1982 with a corresponding decrease in the non-commercial sources of energy (fuel wood, agricultural residues and animal dung). The steep price hike in the commercial energy forms has started showing repercussions on all programmes of development in the country. A further increase in the consumption of commercial forms of energy is bound to aggravate the situation further.

Over 80% of the Indias population lives in sparsely inhabited villages. The order of priority for energy in the rural sector is estimated as follows (Vimal,Tyagi,1984).

Cooking	64%
Agriculture	22%
Village Industries	7%
Lighting	4%
Transportation	3%

The share of different major energy forms to meet the rural energy is as follows:

Non-commercial	65%
Commercial	20%
Human and animal	15%

Of all the conventional forms of energy, electricity, owing to its versatility and convenience of usage is becoming the "most preferred" source of energy. There is an ever-rising demand for power in India. During the last 34 years, 160 billion rupees have been invested in power planning and the power generating capacity has gone up from 2300 MW in 1950 to 40,000 MW in 1984. However, the chronic power shortages are accentuated by not-too infrequent monsoon failures, transport bottlenecks in coal movement and the rising cost of petroleum products. The Seventh Five Year Plan is likely to feature a much larger allocation for power generation than in the previous plans, yet there are far too many constraints and problems which belie any optimism on the power front.

Apart from the non- availability of aluminium, steel, insulators etc., the growth of transmission and delivery system has not matched the expansions of power generation capacity, thereby, affecting both the quality and the reliability of power supply. The present power transmission and distribution losses average 20% as against less than 10% in the developed countries which delude the benefits of the whole grid system (Paul,1983). The major reasons for this enormous wastage, apart from human factors, are the lower density of power demand, longer distances and the low transmission voltages. Consequently, the much talked of "Rural electrification" through central grids may not prove to be quite effective.

At this juncture, it would be worthwhile to have a close look at the problems of the rural electrification programs. Barely 14% of the rural households in the electrified villages make use of electricity and not more than 25% of the wells are energised. The dimensions of rural electrifications are shown below:

Total No. Villages : 584,936
No.of villages electrified (1981-82) : 296,505
No.of pumpsets energised (1981-82) : 4,649,890
Total potential of wells in India : 16,060,000
Target for energised wells(2000 AD) : 11,000,000

For power from a conventional thermal power station, investment costs are between Rs.20,000 and Rs.30,000 per kW (approx. U.S.$ 1500 to $ 2500) for rural electrification. The actual cost of power supply to the consumer in a village is as high as to Rs. 3 (approx.$ 0.28) per kWh, which is at least five times higher than that of the consumer in an urban area. A centralized system not only requires the heavy infrastructural expenditure but also has long gestation period. No doubt, the Indian situation demands new strategies for power generation to provide a modicum of substantial energy supplies to the millions in the countryside.

Of all the newer vistas in power planning, fuel cells offer one of the best and the most effective energy technologies that combats the inherent ills of the central grid system, and many a problem associated with the fossil fuels. Fuel cell power plants can become the most crucial factor in power planning for the urban as well as semi-urban areas and remote inaccessible villages devoid of any infrastructural facilities. Since heavy capital outlays are the major constraints, modular nature of fuel cell could substantially cut down the initial project costs, without affecting efficiency of the system. As the demand increases, these could very conveniently be built up into larger system. Because of ability to convert chemical energy directly into electricity, the rated efficiency of fuel cell is 50-60% in contrast to 30-35% for the conventional systems.

The fuel cell research in India lacks a coordinated effort. The activities of the various groups appear to be scattered in different directions. This paper presents a status of fuel research and potential applications in India.

8.1 Status of Fuel Cell Research in India

There are not many groups in India currently engaged in Fuel Cell research though the first work was initiated in 1974 by the researchers at Central Fuel Research Institute (CFRI), Dhanbad. Mukherjee and coworkers (1981) investigated the techniques for the fabrication of catalyst impregnated carbon electrodes having proper pore size distribution for low temperature H_2-O_2 fuel cell.

Rao and coworkers (1978) of the Indian Institute of Technology, Kharagpur studied the electrochemical oxidation of formamide in acid medium at platinized platinum, platinum-palladium, platinum-tungsten, platinum nickel and platinum gold electrodes using galvanostatic method. They found the catalytic activity of platinum gold alloy electrode better than others with maximum catalytic activity obtained from 35% gold alloy.

Shukla and coworkers (1981) of the Indian Institute of Science, Bangalore attempted to develop a low-cost charcoal based air-electrode for the direct/ indirect type ammonia-air fuel cells. Indirect ammonia air fuel cells could be a feasible system for larger units from basic thermodynamic considerations of maximum free utilization as only a part of the energy will be utilized in heating the cracking unit; whereas the direct ammonia air fuel cell would be economical for small-scale, low-power, long-life application. The progress to date on this work is not known.

Venkatesan and coworkers (1981) of the Central Electrochemical Research Institute, Karaikudi have considered developing a 1 kW low temperature alkaline H_2-O_2 fuel cell as well as high temperature molten carbonate and solid electrolyte fuel cells operating at temperatures above 700°C. They have fabricated and tested single cells consisting of electrodes of three layer DSK type and having area of 15 cm^2 (SC-I) and 30 cm^2 (SC-II). The SC-I showed a cell voltage of 0.70 V at current density of 0.035 Amp/cm^2 at 60°C while the SC-II showed a cell voltage of 0.75 V at current density of 0.015 Amp/cm^2 at 50°C. They have also assembled 30 fuel cell modules consisting of two cells, three cells, four cells or six cells. A number of two, three and four cell modules tested at room temperature showed a satisfactory performance for periods ranging from 2000 hours to 7500 hours at current densities in the range of 0.015 to 0.30 Amp/cm^2.

Notable contributions have been made by Govil and coworkers (Govil,1982; Phadke,1983; Sonawat,1984; Sonawat 1984; Phadke,1984) of the Tata Institute of Fundamental Research (TIFR), Bombay in the area of biochemical fuel cell. The biochemical fuel cell is a device which converts the chemical energy of a hydrogen rich fuel such as alcohol, glucose, hydrocarbons or hydrogen itself into electrical energy through enzyme catalyzed oxidation reduction reactions. The major difficulty in the design of such systems is the slow electron transport from the substrate to the electrode. The theoretical studies of Govil et al (Phadke,1983) involving molecular orbital calculations on the electron flow diagrams of flavin adenine dinucleotide (FAD) or nicotinamide adenine dinucleotide (NAD) rings during their oxidation-reduction cycle showed that it is possible to obtain efficient electron transport from the coenzyme to the electrode surface by immobilizing FAD or NAD through semiconducting side chains at certain selected positions to the electrodes. Based upon these studies Govil et al (Sonawat,1984) have designed a coenzyme-immobilized anodes which show the expected redox cycles in cyclic voltametric studies. They have succeeded in chemically linking FAD via a carbon bridge to Teflon-bonded carbon black and the subsequent immobilization of glucose oxidase on the FAD modified electrodes. Glucose oxidase converts glucose into gluconic acid and releases two electrons during this process. The TIFR team is investigating the potential of such an electrode for use in a biochemical fuel cell.

Banerjee (1984) at the University of Delhi has initiated a research program to investigate the suitability of various low temperature H_2-O_2 fuel cell for low cost power supply. Vasudevan and coworkers (1985) at the Indian Institute of Technology, New Delhi plan to synthesize a variety of electrocatalysts such as Phthalocyanines of Fe, CO, and Ni and study their activity in the electrochemical oxidation. Pandya, Varshney and Gopalan (1985) of the Tata Energy Research Institute, New Delhi also plan to develop an experimental single fuel cell for electrode kinetic investigations of fuel cell reactions. Pachauri and Pandya (1985) at the Tata Energy Research Institute, New Delhi plan to carry out a site specific techno-economic analysis through demonstration project to assess feasibility of fuel cell technology. It is felt only through such a detailed evaluation tnat specific areas will be revealed wherein major modifications, improvements and economies can be brought about to make the use of fuel cell technology a viable alternative in India.

8.2 Scope of Fuel Cell Applications and Development in India

India is predominantly an agricultural country with 80 of its population living in more than half a million villages. Major emphasis is now being laid on utilization of renewable forms of energy such as biomass. India produces annually 200 millions tons of agricultural residue such as wheat straw, rice hulls, nut shells etc. This biomass is mainly organic in nature, a substantial portion of which is cellulose, which can be converted into gaseous (methane) or liquid (methanol, ethanol) fuels by biological processes like anaerobic digestion and fermentation. This enzymatic breakdown of biomass at low pressure and low temperature is accomplished by using specific microorganisms such as Cellulomonas sp, Acetovibrio Cellutolyticus, Bacteriodes succinogenes or any other several Methanogens.

In rural areas, the biogas can not only serve for cooking, but can also be utilized for lighting and powering small diesel engines. In the context of a vast network of biogas plants in India, dovetailing of the fuel cell technolcgy into the simple biogas system could mean a self sustained decentralized energy system catering effectively to the diverse consumption needs of a particular area, howsoever low the load factor may be. The alluring proposition of coupling of biogas with fuel cells should be examined in India through actual engineering, installation and evaluation of such a system. The power generated through such a system can be utilized for rural electrification, irrigation, cottage industries, farming and canning. In large metropolises such as Bombay and Delhi, sewage is readily available which can also be utilised to produce the gaseous or liquid fuels mentioned above by the action of a wide range of micro-organisms.

Other potential applications of fuel cells are for storage of electricity produced during off peak hours at the conventional power stations, for military establishments in remote areas, for submarines, for space satellite and for specialised applications like computers and radar installations in regions where power fluctuations and breakdowns are frequent. Finally, the shortcomings and advantages of fuel cell technology in the Indian context should be evaluated by field application and demonstration. Based upon such studies it will not only be possible to determine the limits of economic viability with existing technology but will also be possible to identify areas for further research and development necessary for the widespread diffusion of fuel cell technology in India.

9.0 BIBLIOGRAPHY

ADLHART, O. in CONSIDINE, D.M. (Ed.) (1977) "Fuel Cells" in "Energy Technology Handbook". McGraw Hill, New York.

ANGRIST, S.W. (1982) "Direct Energy Conversion". Allyn and Bacon Inc., Boston.

ARCHER, D.H. in YOUNG, G.J. and LINDER, H.R. (Ed.) (1965) "Fuel Cell Systems - Advances in Chemistry Series". American Chemical Society, Washington DC, p. 332-343.

AUSTIN,L.G. in YOUNG,G.J. (Ed.) (1960) "Electrodes Kinetics of Low Temperature Hydrogen - Oxygen Fuel Cells" in Fuel Cells. Reimhold Publishing Corporation, New York.

BANERJEE, A.N. (1984) "Search for Economical Low Temperature Fuel Cells". Annual Report, Department of Non-Conventional Energy Sources.

BELL, R.A. and MESSNER, W.A. (1980) "Fuel Cells for Electric Utility Use". Proc. 7th, Energy Technical Conference, Washington, March 4-26, p. 964-973.

BOCKRIS, J.O.M. and SRINIVASAN, S. (1969) "Fuel Cells: Their Electrochemistry". McGraw Hill, New York.

BORYS, S.S. and ACKERMAN, J.P. (1979) "Molten Carbonate Fuel Cell Systems Development Program". Proc. 14th Intersociety Energy Conversion Engineering Conference (IECEC), Boston, August 5-10, p. 563-567.

BUSBY, R.L. (Ed.) (1984) March/April, Gas Research Institute Digest, Chicago.

CARL, B. (Ed.) (1968) "Handbook of Fuel Cell Technology". Prentice Hall Inc., New Jersey.

EISENBERG, M. in TOBIAS, C.W. (Ed.) (1962) "Design and Scale-up Considerations of Electrochemical Fuel Cells" in Advances in Electrochemistry and Electrochemical Engineering Vol.2. Interscience, New York.

FEDUSKA, W. and ISENBERG, A.O. (1983) "High Temperature Solid Oxide Fuel Cell-Technical Status". J.Power Sources, Vol.10, p. 89-102.

PICKETT, A.P. (1978) December, "Fuel Cell Power Plants". Scientific American, Vol.239, No.6.

GALLAGHER, G.E. (1983) "Fuel Cells and University Research". Report (RL-83-09), Science and Engineering Research Council, Rutherford Appleton Laboratory, Oxfordshire.

GLASSTONE, S. (1983) "Energy Deskbook". Van Nostrand Reinhold Inc., New York.

GOVIL, G. and SARAN, A. (1982) November, "Biochemical Fuel Cells". J.Indian Chem.Soc., Vol.LIX, p. 1226-1228.

GREHIER, A., BREELLE, Y., CHERON, J., DEGOBERT,P.(1979) "Fuel Cells; Research and Development-Current Program and Outlook". Report PV N^{o} 26761, N^{o} de project: L61-00 401, Institut Francais du Petrole, France.

ISAACS, H.S. (1981) Nov. 16-18, "Solid Electrolyte Fuel Cells". Proc.Fuel Cells - Technology Status and Applications Symp., Chicago, p. 83-107.

ISENBERG, A.O. in MUNTYRE, J.D.E., SRINIVASAN, S. and WILL, F.G. (Ed.) (1977) "Electrode Materials and Processes for Energy Conversion and Storage". The Electrochemical Society, Princeton, p. 572.

ITOH, N. and OGURA, Y. (1984) "Japanese National R. D and D Program for Developing Fuel Cells". Progress in Batteries and Solar Cells, Vol.5, p. 290-293.

KORDESH, K.V. (1978) March, "25 Years of Fuel Cell Development (1951-1976)". J.Electrochem. Soc., Vol.125, No.3.

LANDGREBE, A.R. and WEINSTOCK, I.B. (1981) May "Application of Electrochemical Technologies in the Utility Industry". Modern Power Systems, Vol.1, No. 5, p. 42-51.

LARSON, E.(1980) "Fuel Cells in the Gas Industry". Proc., 7th Energy Technology Conference, Washington, p. 974-982.

LEUCKEL, W.J. and CASSERLY, J.P. (1976) March 26-31, "Fuel Cells for Utility Service". Proc. 3rd Energy Tech.Conf., Washington, p. 183-194.

LIEBHAFSKY, H.A. and CAIRNS, E.J. (1968) "Fuel Cells and Fuel Batteries". McGraw Hill, New York.

LINDEN, D. (Ed.) (1984) "Handbook of Batteries and Fuel Cells". McGraw Hill, New York.

LOFTNESS, R.L. (Ed.) (1984) "Energy Handbook". Van Nostrand Reinhold, New York.

MARSHALL, E. (1984) "The Procrastinator's Power Source". Science, Vol. 224, No. 4646, p. 268-270.

MCDOUGALL A. (1976) "Fuel Cells". Macmillan Press, London.

MOORE, W.J. (1962) "Physical Chemistry". Prentice Hall Inc., New Jersey,

MUKHERJEE, P.N., BHAT, D.M., GHOSH, S.P., CHATTERJEE, D.S. PAL,M. and ROY, T.N. (1981) "Carbon electrodes for Low Temperature H_2/O_2 Fuel Cell". Central Fuel Research Institute, Dhanbad, Annual Report of the Council of Scientific and Industrial Research, New Delhi.

NUTTAL, L.J. and MCELORY, J.F. (1983) "Status of Solid Polymer Electrolyte Fuel Cell Technology and Potential for Transportation Applications". Int.J.Hydrogen Energy, Vol.8, No.8, p. 609-615.

PACHAURI, R.K. and PANDYA, J.D. (1985) "On-site Integrated Energy Systems : Fuel Cell Coupling with Biogas". Research Proposal, Tata Energy Research Institute, New Delhi.

PANDYA, J.D. and VARSHNEY, S. and GOPALAN, P. (1985) "Development of an Experimental Single Fuel Cell for Electrode Kinetic Studies and Performance Evaluation". Research Proposal, Tata Energy Research Institute, New Delhi.

PARKINSON, G., (1983) Jan.24, "Fuel Cell's Prospects are Getting Brighter". Chemical Engineering, p. 30-35.

PAUL, S. (1983) "Newer Vistas in the Third World Energy Management-Fuel Cells, Biogas Hybridization and Bogs". Energy Management, Vol. 7, No.3, p. 239-250.

PHADKE, R.S., SONAWAT, H.M., and GOVIL, G. (1983) "Electron Delocalization During the Oxidation Reduction Cycle of FAD and NAD : A Quantum Chemical Approach to the Design Coenzyme - Immobilized Bioanode for Biochemical Fuel Cells". Int.J. Quantum Chem., Quantum Bio., Symp. 10, p. 251-262.

PHADKE, R.S., SONAWAT, H.M. and GOVIL, G. (1984) "Fuel Cell Power". Science Age, Vol. 2, No. 9, p. 28-31.

PIERCE, R.D. (1981) Nov.16-18, "Molten Carbonate Fuel Cells - Technology Status". Proc. Fuel Cells: Technology Status and Applications Seminar Symp., Chicago, p. 67-81.

RAO, K.V., DAS, S.C. and ROY, C.B. (1971) "Electrocatalysis by Alloy Electrodes: Oxidation of Formamide". J.Electrochem. Soc.India, Vol.27, No.3, p. 135-139.

ROHR, F.J. in HAGENMULLER, P. and VAN GOOL, W. (Ed.) (1978) "Solid Electrolytes". Academic Press, New York, p. 431.

RUKA, R.J. in SRINIVASAN, S., SALZANI, F.J. and LANDFGREBE, A.R. (Ed.) (1978) "Industrial Water Electrolysis". The Electrochemical Society, Princeton, p. 56.

SANGHVI, A.P. in PACHAURI, R.K. (Ed.) (1980) "International Energy Studies". Wiley Eastern, New Delhi, p. 383-392.

SELMAN, R.J. (1981) Nov.16-18, "Fuel Cells : Fundamentals and Types - Unique Features". Proc. Fuel Cells - Technology Status and Applications Seminar, Chicago, p. 1-31.

SHUKLA, A.K., SATHYANARAYANA, S. and RAO, C.N.R. (1981) Indian Institute of Science, Bangalore, Directory of Research Projects on Renewable Sources of Energy, Department of Science and Technology, New Delhi.

SIMONS, S.N., KING, R.B., PROKOPIUS, P.R. (1981) "Phosphosic Acid Fuel Cells Technology Status". National Aeronautics and Space Administration, Ohio, DOE/NASA/17088-3, NASA TM-82791.

SONAWAT, H.M., PHADKE, R.S., and GOVIL, G. (1984) "Covalent Immobilization of FAD and NAD Glucose Oxidase on Carbon Electrodes". Bio tech.Bio.Eng., Vol. XXVI, p. 1066-1070.

SONAWAT, H.M., PHADKE, R.S., and GOVIL, G. (1984) "Towards Biochemical Fuel Cells". Proc. Indian Acad. Sci. (Chem.Sci.), Vol.93, No. 6, p. 1099-1107.

SRINIVASAN, S. and ISAACS, H.S. (1979) Aug. 5-10, "Solid Electrolyte Fuel Cell for Electric Utility Power Generation". Proc. 14th IECEC, Boston, p. 568- 575.

TOBIAS, C.W., EISENBERG, M. and WHITE, C.R. (1952) "Diffusion and Convection in Electrolysis - A Theoretical Review". J.Electrochem Soc., Vol.99, p. 359C.

VASUDEVAN, P. (1985), Personal Communications.

VENKATESAN, V.K. and others (1981) "Development of 1 KW Low Temperature H_2/O_2 Fuel Cell". Central Electrochemical Research Institute, Karaikudi, Research Projects on Renewablel Sources of Energy Directory, Department of Science and Technology, New Delhi.

VIMAL, O.P. and TYAGI, P.D. (1984) "Energy from Biomass". Agricole Publishing Academy, New Delhi.

WEISBART, J. and RUKA, R.J. in YOUNG, G.J. (Ed.) (1963) "Fuel Cells". Vol. 2, Reinhold, New York, p. 37.